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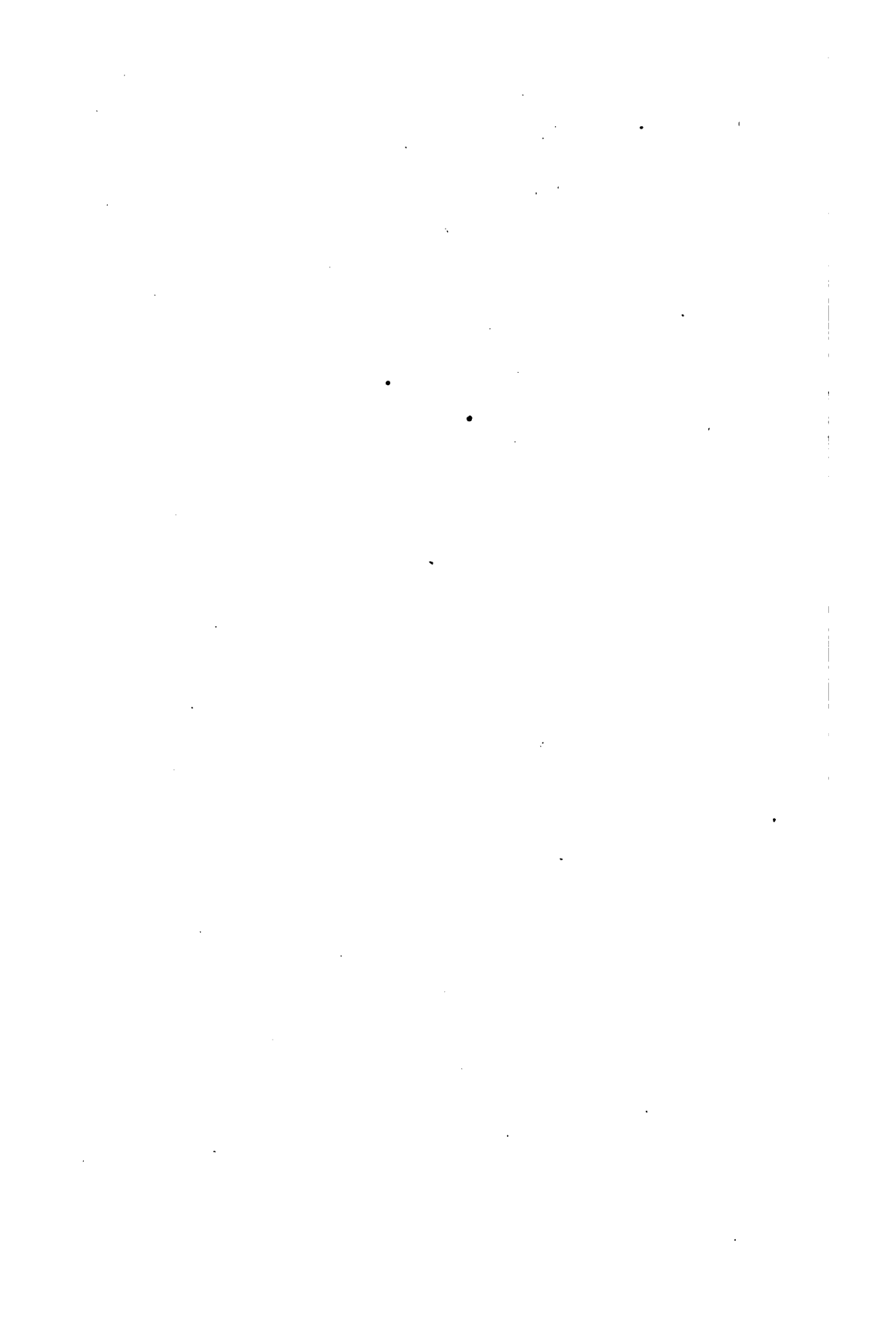
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HAND BOOK
OF
QUALITATIVE CHEMICAL ANALYSIS.

SELECTED AND ARRANGED FOR THE

Students of the State Agricultural College of Michigan,

BY

ROBERT C. KEDZIE, A. M., M. D.,

PROFESSOR OF CHEMISTRY.

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INORGANIC CHEMICAL ANALYSIS.

THE object of Chemical Analysis is to ascertain the chemical composition of any given body. Inorganic chemical analysis is divided into Qualitative Analysis and Quantitative Analysis. Qualitative Analysis is the separation of the chemical components of any substance, either in a separate form or in some known state of chemical combination. It is also used to identify simple or elementary substances by bringing them into chemical combination with other substances whose chemical composition is already known. Qualitative Analysis teaches us to separate and identify the components of any substance with regard to their quality only, without regard to their quantity, and answers the question, "*What* does the substance contain?" Quantitative Analysis furnishes the methods of procedure by which we determine the relations of weight or volume which these elements bear to each other, and answers the question, "*How much* of its several given elements does the substance contain?"

The methods of Qualitative Analysis consist in bringing the substance under examination into contact with other bodies of known properties, and observing the phenomena which ensue. These phenomena consist in alterations, either in state of aggregation, form or color, depending upon chemical change. By exhibiting the constituent parts of a substance of *unknown* composition, in forms of *known* composition, the constitution of the body examined, and the presence of its several component elements may be positively inferred. The separation and identification of substances are usually accomplished by physical changes. All bodies which we employ for the purpose of producing physical changes by chemical transformations we call *reagents*; and the resulting changes are called *reactions*. Acids, bases, salts, and elementary bodies are alike used as reagents. The reader will note a difference between *analysis* and *testing*: we test for any particular substance by eliciting some property peculiar to itself, such as a change of color (*e.g.*, the blood-red coloration formed by adding a sulphocyanide to a solution of ferric salt), or the production of a peculiar odor (*e.g.*, the garlic odor of the vapor of metallic arsenic).

By means of reagents the chemist interrogates the substance under examination, inquiring whether it contains this or that group of chemically similar elements, or only this or that member of such group. If the question be put correctly, that is, if all the conditions under which the reaction expected can be produced by the reagent employed, i.e. carefully observed, the answer is decisive as to the presence or absence of the element or group of elements sought. But if the properties and chemical relations of the bodies formed by the chemical changes which constitute the reaction, have been wholly or partially neglected, the answer is at least of doubtful accuracy, if not certainly erroneous.

Chemical substances act upon each other more certainly and speedily when they are in the *fluid state*, because the contact of the molecules is then more complete, and that interchange of particles which constitutes the reaction more easily effected. The fluid state may be secured either by *solution* or by *fusion*. Reagents, therefore, may be employed either in the *wet way* or in the *dry way*. In the *wet way* the reagent in solution is brought into contact with the substance to be analyzed, which is usually in the liquid form. In the *dry way* the substance to be analyzed and the reagent are brought together in the solid state and subjected to a heat sufficient to melt the reagent, or both the reagent and the assay. At a high temperature chemical reactions are secured similar to those obtained by solution: certain changes are also secured by the addition or abstraction of oxygen, according as we use the oxidizing or deoxidizing flame. The knowledge derived in the *dry way* by the use of the blowpipe, and by the behavior of bodies in the different flames which can be produced by it, is one of great importance in Qualitative Analysis. This method is mainly employed in the preliminary examination, and the details of manipulation in the *dry way* are described in connection with the preliminary examination.

Many reagents exhibit the same or similar behavior with a group of chemically similar elements, and with most of the compounds of these elements; and can therefore be used to divide the elements into groups. Such reagents are called *group reagents*. Others serve for the further distinction of the several members of such groups, and are termed *special reagents*. Their selection depends upon the knowledge of the behavior of such reagents to each single element of the group, or of each of its several compounds. The number of special reagents is much greater than that of the group reagents, their nature being as various as that of the substances which come under examination. Their selection depends on the solubility or insolubility, color, or other physical or chemical properties of the new compounds to which they give rise. Certain special reagents produce reactions which are entirely characteristic of a given substance or compound. Such reagents and reactions are distinguished by being printed in SMALL CAPS.

It is the task of the analyst not only to establish that this or that body is present in a compound, but he is to prove that no other body is present beside those which he has actually found. Hence it is evident that he must not treat the substance under examination with reagents indiscriminately. He must follow a certain fixed order, a methodical system in the application of reagents. This systematic method consists in the employment of group reagents for the successive separation of groups of elements possessing certain common chemical properties, and finally, in the recognition of each member in such group by the use of special reagents which are characteristic.

The first thing to be done in the Qualitative Analysis of a solid body is to subject it to a preliminary examination in the *dry way*, whereby important information as to its composition may often be obtained. The substance is then dissolved and its constituents determined by analysis in the *wet way*. The course of Qualitative Analysis therefore embraces three parts:

- I. Preliminary examination in the *dry way*.
- II. Solution, or conversion into the liquid form.
- III. Analysis of the solution in the *wet way*.

TABLE I.

The substance under examination is non-metallic, being neither a metal nor an alloy.

Reduce the substance to a fine powder in a porcelain mortar.

FIRST STEP.

Place a few grains of the substance in a clean, dry test tube, and heat, at first gently, but if no change ensues, to a full red heat, and watch the changes.

Substance unaltered.	Absence of organic matter; volatile bodies; fusible bodies; salts containing water of crystallization; salts containing interstitial water; substances whose color is changed by heat.
Changes color.	Many metallic oxides; White to yellow, h., to white, c., ZnO. White to yellowish brown, h., to dirty white, c., SnO. Yellow to brownish red, h., to yellow, c., PbO. White to orange red, h., to yellow, c., Bi ₂ O. Red to black, h., to red, c., Fe ₂ O. Brown to black, h., to red, c., Fe ₂ O ₃ .8H ₂ O. Black after intense heating, salts-of Co. and Cu.
Aqueous vapors are expelled.	Substances containing water of crystallization; holding water mechanically enclosed (decrepitate); decomposable hydrates (alum and borax intumesce.)
Sublimate forms.	Gray tarnish or distinct globules easily united, Hg. Substance melts, sublimes, giving crystalline sublimate white, c.,—probably HgCl. Sublimes without melting, sublimate yellow, h., white, c., Hg ₂ Cl. White sublimate without melting or changing color, evolving ammoniacal odor and the vapor changing red litmus to blue when heated with Na ₂ CO ₃ —some salts of ammonia; White sublimate without melting or changing color, octohedral crystals (use lens) As ₂ O; Substance melts, emits dense white vapors, forming crystalline sublimate which gives a strong acid reaction with blue litmus paper, H ₂ C ₂ O ₄ .2H ₂ O.; Reddish-brown drops, S.; Black sublimate, becoming red by rubbing with glass rod, HgS.
Carbonization.	Organic bodies; Cyanogen compounds. Blackening is not necessarily carbonization—usually a burnt odor and escape of combustible gases. The organic substances burn vividly when heated in test tube with KNO ₃ , with formation of K ₂ CO ₃ .

TABLE I.—FIRST STEP, CONTINUED.

Gases escape when strongly heated.	<p>O.—from Nitrates, Chlorates, Bromates, Iodates, and peroxides (ignites spark on splinter);</p> <p>SO₂.—from Sulphates, Sulphites, Hyposulphites, or oxidation of Sulphur or Sulphides (odor of burning sulphur);</p> <p>NO₂.—from decomposition of the Nitrates of all metals except the alkalis (reddish-brown fumes);</p> <p>CO₂.—from decomposition of carbonates (lime water);</p> <p>CN₂.—from decomposition of metallic Cyanides (odor and peach blossom flame);</p> <p>H₂S.—from Sulphides containing water (odor and lead paper);</p> <p>NH₃.—from salts of ammonia, and some Cyanogen compounds (odor and alkaline reaction with red litmus paper).</p>
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SECOND STEP.

A moistened Platinum wire is dipped into the powdered substance and strongly heated in the reducing flame. (Should the previous examination indicate the presence of any fusible metal, *e.g.*, Pb, Sb, Bi., the experiment under this step should be omitted entirely, or a thread of asbestos used in place of the Platinum wire.)

Colors the flame	Yellow	<p>{ Sodium.</p> <p>{ Molybdic troxide—greenish yellow.</p> <p>{ Substances rich in carbon.</p>
	Red	<p>{ Strontium (carmine.)</p> <p>{ Calcium (orange red.)</p>
	Green	<p>{ Copper (excepting CuCl₂) bright green.</p> <p>{ Barium, yellowish green.</p> <p>{ Molybdic acid, yellowish green</p> <p>{ Boric acid, " "</p> <p>{ Phosphoric acid, bluish "</p>
	Blue	<p>{ Lead.</p> <p>{ Arsenic.</p> <p>{ Chloride, Bromide and Iodide of Copper.</p> <p>{ Antimony (greenish blue.)</p>
	Violet	<p>{ Potassium (easily obscured.)</p> <p>{ Cyanides (peach-blossom.)</p>

THIRD STEP.

A few grains of the substance are placed on charcoal and heated in the reducing flame.

Volatile (without incrustation or the formation of metallic globule.)	<p>Salts of NH₄;</p> <p>As₂O₃ (odor of garlic);</p> <p>Some compounds of Hg.</p>
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TABLE I.—THIRD STEP, CONTINUED.

Volatile (or partially volatile) with incrustation.	Incrustation yellow, c.—PbO Incrustation dark yellow, c.—Bi ₂ O ₃ . Incrustation white, c.—Sb ₂ O ₃ . Incrustation blue and yellow—MoO ₃ . Incrustation reddish-brown, or a variegated tarnish—CdO. Incrustation yellow, h. white, c.—ZnO. Incrustation difficult to volatilize, yellowish, h. dirty white, c.—SnO ₂ .
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NOTE.—Many substances which sublime in the test tube under *First Step*, will give an incrustation when treated on charcoal, but these incrustations should be disregarded, and the indications from the sublimation followed.

Fusible, non-volatile, absorbed by the coal or forms a bead. (Residue pressed on moistened turmeric paper stains it brown.)	Compounds of { K. Na. Si. Ba. Sr. Some Salts of Ca.
Infusible and color unchanged.	SiO ₂ . Al ₂ O ₃ . Some compounds of { Ba. Sr. Ca. Mg. Luminous when heated intensely.

FOURTH STEP.

Place some of the substance on charcoal and heat in Reducing flame, moisten with a drop of Co₂(NO₃), then heat again intensely.

Colored Mass—(color best observed when assay is cold.)	<table> <tr> <td data-bbox="491 1107 609 1142">Blue glass</td><td data-bbox="615 1090 826 1159">{ alkaline Phosphates " Borates " Silicates</td></tr> <tr> <td data-bbox="491 1177 609 1229">Blue mass. (infusible).</td><td data-bbox="615 1177 791 1229">{ Al₂O₃ SiO₂—(pale blue)</td></tr> <tr> <td data-bbox="491 1263 556 1289">Green</td><td data-bbox="615 1237 856 1307">{ ZnO. yellowish green c. SnO₂. bluish green c. Sb₂O₃ dirty green c.</td></tr> <tr> <td data-bbox="491 1307 603 1333">Pink</td><td data-bbox="615 1307 697 1333">MgO.</td></tr> </table>	Blue glass	{ alkaline Phosphates " Borates " Silicates	Blue mass. (infusible).	{ Al ₂ O ₃ SiO ₂ —(pale blue)	Green	{ ZnO. yellowish green c. SnO ₂ . bluish green c. Sb ₂ O ₃ dirty green c.	Pink	MgO.
Blue glass	{ alkaline Phosphates " Borates " Silicates								
Blue mass. (infusible).	{ Al ₂ O ₃ SiO ₂ —(pale blue)								
Green	{ ZnO. yellowish green c. SnO ₂ . bluish green c. Sb ₂ O ₃ dirty green c.								
Pink	MgO.								

FIFTH STEP.

Mix some of the finely powdered substance with twice that amount of dry Na_2CO_3 , place on charcoal and heat strongly in the Reducing flame, (a mixture of KCy and Na_2CO_3 is a powerful reducing agent and should be used in treating compounds of Sn .)

Metallic globule with incrustation.	White incrustation. Globule easily formed and volatilized—brittle— Sb . Slight white incrustation. Globule formed with difficulty, malleable, Sn . Yellow incrustation. Globule easily formed—soft, very malleable. Pb . Yellow incrustation. Globule easily formed, very fusible, brittle. Bi .
Metallic globule without incrustation.	Red globule, Cu . Yellow globule, Au . Silvery-white globule, Ag . <div style="display: inline-block; vertical-align: middle; margin-left: 10px;"> } Malleable. </div>
Metallic powder or grains without incrustation.	Infusible and Magnetic, Fe.Ni.Co . Infusible and non-Magnetic, Pt.Ir.W .
Incrustation without metallic grains or globule.	White, very volatile, odor of garlic— As . Yellow h. white c.— Zn . Dark red, or variegated— Cd .



TABLE I.—CONTINUED.

SIXTH

Form a clear bead by fusing the flux on a loop of Pt. wire. The bead is then and then in the reducing flame.

(In the following table h. signifies hot; c., cold; S.S., strongly saturated often varies with the temperature

Color of Beads.	WITH BORAX.	
	IN OXIDIZING FLAME.	IN REDUCING FLAME.
Colorless, h. and c.	<p>With any amount { Silica which the bead { Alumina will dissolve. { Stannic oxide { Oxide of Silver S.S. { Baryta } Opaque by { Strontia } flaming { Lime { Magnesia }</p> <p>N.S. oxides of { Antimony { Bismuth { Cadmium { Indium { Lead { Zinc.</p>	<p>With any amount { Silica. which the bead will { Alumina. dissolve. { Stannic oxide. { Baryta S.S. { Strontia } Opaque { Lime } by { Magnesia } flaming { Manganic oxide S.S. (opaque red c.: oxide of copper.) N.S. oxides of { Antimony { Bismuth { Cadmium { Lead (Gray at first { Nickel from finely re- { Silver duced metals, { Zinc. becoming clear as blast is continued.)</p>
Gray and cloudy, c.		<p><i>On Charcoal.</i></p> <p>Oxides of { Antimony { Bismuth { Cadmium { Lead { Silver { Zinc { Nickel.</p>
Yellow, h.	<p>S.S. colorless, c. { Cadmium } Opaque by { Zinc } flaming S.S. colorless, c. { Antimony { Bismuth { Lead.</p> <p>Feebly saturated, { Ferric oxide (more or less col- { Uranic oxide orless, cold.) { Chromic oxide (yellowish green c.)</p>	<p>S.S. yellow { Titanic acid. to brown { Enamel blue by flaming. Yellow to { Tungstic acid. dark brown, c. { Brown to { Molybdic acid. opaque c. {</p>

STEP.

TABLE I.—CONTINUED.

dipped into the finely powdered assay and heated, first in the oxidizing flame

with the assay; N.S., not completely saturated. The color of the bead and the amount of assay used.)

WITH MICROCOSMIC SALT.	
IN OXIDIZING FLAME.	IN REDUCING FLAME.
Undissolved, Silica (skeleton). Soluble with difficulty { Alumina. { Stannic oxide. S.S. { Baryta } { Strontia } Opaque by flaming. { Lime } { Magnesia } N.S. oxides of { Antimony { Bismuth { Cadmium (Yellowish, h., when S.S., or Indium { Lead { Zinc. (colorless, c.)	Undissolved Silica (skeleton) Soluble with { Alumina { Stannic oxide. { difficulty S.S. { Baryta } { Strontia } Opaque by { Lime } flaming. { Magnesia } { Manganic oxide. S.S. oxide of { Antimony { Bismuth { Indium (Gray at first from finely reduced metal, becomes clear as blast is continued.) { Cadmium { Lead { Silver { Zinc.
	<i>On Charcoal.</i> As with Borax. Most readily with tin.
S.S. oxides of { Antimony { Bismuth { Cadmium (colorless, c.) { Lead { Zinc. Yellowish opalescent, c., oxide Silver. Feebly saturated { Ferric oxide { (S.S. red h., yellow, c.)	Violet, c. { Titanic acid. Yellow to red h. { Ferric oxide. { (on cooling, at first greenish, then reddish.) Blood red c. { Titanic, and { Tungstic acids { containing iron.

TABLE I.—CONTINUED.

SIXTH STEP,—

Color of Beads.	WITH BORAX.	
	IN OXIDIZING FLAME.	IN REDUCING FLAME.
Red to Brown, h.	Yellow, c. { Ferric oxide Ceric oxide Uranic oxide. S.S. { Chromic oxide (yellowish green, c.) Oxide of Iron containing Manganese (yellowish red, c.)	Oxide Copper reduced to Cu_2O .—red, c.
Violet, h.	Red, c., Manganic oxide Reddish brown, c. { Oxide of Nickel containing Cobalt. Oxide of Cobalt containing Manganese.	
Blue, c.	h. and c. { Oxide Cobalt S.S. (green h.) { Oxide Copper	h. and c. { Oxide Cobalt
Green, h.,	Blue, c., Oxide of Copper. Ferric oxide, containing Cobalt or Copper, and oxide of Copper containing Iron or Nickel (the green color changes on cooling, according to the saturation, as well as the proportions in which the oxides are present, to light green, blue or yellow.)	Yellowish or bottle green c. { Ferric oxide Light to dark emerald green, according to saturation. { Chromic oxide h. and c. black by flaming Uranic oxide
Green, c.	Yellow to red, h. { Chromic oxide	h. and c. { Chromic oxide. (emerald green)

CONTINUED.

TABLE I.—CONTINUED.

WITH MICROCOSMIC SALT.	
IN OXIDIZING FLAME.	IN REDUCING FLAME.
S.S. yellow c. { Ferric oxide Ceric oxide. Reddish yellow, c., Nickle oxide Emerald green, c., Chromic oxide.	
Manganic oxide	Titanic oxide, cold bead violet, hot bead yellowish.
h. and c. { Oxide cobalt S.S.(green h.) { Oxide Copper	h. and c. { Oxide Cobalt. Brownish h. { Tungstic acid.
Blue c. Oxide of Copper. Ferric oxide containing Cobalt or Copper, and oxide of Copper containing Iron or Nickel (the green color changes on cool- ing, according to the saturation, as well as the proportions in which the oxides are present, to light green, blue or green.) Yellowish green. Molybdic acid.	Uranic oxide.
Reddish h. { Chromic oxide (emerald green) Yellowish h. { Uranic oxide (yellowish green)	Yellowish green, h., Uranic oxide, Dirty green, h., Melybdic oxide. Reddish, h., Chromic oxide.

TABLE II.

Preliminary Examination of Metallic Substances and Alloys.

Heat on charcoal in the reducing flame.	<p>Volatilized rapidly without fusing, forming white fumes, coloring the flame bluish, and giving the odor of garlic—As.</p> <p>Readily volatilized without fumes or distinct odor, and not coloring the flame—Hg.</p> <p>When strongly ignited burning with bluish-white blaze, forming incrustation on coal, yellow h. white c.—Zn.</p> <p>Readily fusible, very malleable, so soft that it can be cut by finger nail, burning with sky-blue flame, giving yellow incrustation c.—Pb.</p> <p>Rosy-white metal, very brittle, not coloring the flame, giving yellow incrustation c.—Bi.</p> <p>White, crystalline, very brittle metal, giving a greenish-blue flame, forming a white incrustation c.—Sb.</p> <p>White malleable metal, cannot be cut by finger nail, very fusible, not coloring flame, giving white incrustation difficult to volatilize. Sn.</p> <p>White malleable metal, not coloring flame, forming no incrustation on coal or only a slight red incrustation—Ag.</p> <p>Tinges oxidizing flame green, gives no incrustation and forms red malleable globule—Cu.</p> <p>Infusible, strongly magnetic—Fe.Co.Ni.</p> <p>Infusible, non-magnetic—Pt.Ir.W.</p>
Heat some of the substance in a test tube to red heat.	<p>Gray sublimate in cold part of the tube which may be united into silvery drops by rubbing with a glass rod—Hg.</p> <p>If there is no gray sublimate formed, absence of Hg.</p> <p>Dark Mirror on cooler part of the tube, becoming white and crystalline by repeated sublimation—As.</p> <p>Volatilizes at red heat and forms solid shining globules on cold part of tube—Cd.</p>

TABLE III.

Behavior of the Alkalies before the

	HEATED ON CHARCOAL.	COLORS FLAME.
Potash Compounds.	Fusible, non-volatile, absorbed by coal, or forms a bead.	Violet, easily obscured by other salts.
Soda Compounds.	Fusible, non-volatile, absorbed by coal or forms a bead.	Yellow, very intense.
Ammonia Compounds.	Volatile and absorbed by the coal.	Faint green flame when strongly heated; best seen in darkened room.

TABLE IV.

Behavior of Earths alone, and

	ALONE ON CHARCOAL AND IN THE FORCEPS.	WITH BORAX ON PLATINUM WIRE.
Alumina Al_2O_3 .	Unaltered.	Dissolves slowly to a clear bead, becoming opaque neither by flaming nor saturation. When much is added in fine powder the bead is cloudy, scarcely fusible, and shows a crystalline surface on cooling.
Silica SiO_2 .	Unaltered.	Dissolves slowly to a clear difficulty fusible bead, that cannot be made opaque by flaming.

TABLE III.

blowpipe with certain reagents.

OTHER TESTS.
In presence of Soda compounds, Potash may be recognized by making a borax bead, adding a small quantity of boric acid, then adding Oxalate of Nickel to form a brown bead. Fusing any Potash compound with this bead will produce a fine blue bead best seen when cold.
In absence of Soda compounds the Nickel bead described above gives a brown color.
Any compound of Ammonia heated with Na_2CO_3 in test tube evolves ammonia, recognizable by odor, alkaline reaction, and white fumes with HCl.

TABLE IV.

with reagents before the blowpipe.

WITH MICROCOSMIC SALT ON PLATINUM WIRE.	WITH Na_2CO_3 ON CHARCOAL.	WITH SOLUTION OF Co_2NO_3 IN O.F.L.
Dissolves slowly to a clear bead, that is always clear. When much is added the undissolved portion becomes semi-transparent.	Swells a little, and forms an infusible compound, and the excess of soda goes into the coal.	After a <i>strong</i> blast assumes a fine blue color, the intensity of which is only properly apparent on cooling.
Dissolves only in very small quantity to a clear bead. The undissolved portion floats as a semi-transparent skeleton in the melted bead.	Dissolves with a lively effervescence to a clear bead.	With a little solution assumes a feeble bluish color, becoming a dark gray with more. The thinnest edges can be fused to a reddish blue glass in a <i>very</i> hot flame.

TABLE V.

Behavior of alkaline earths, alone and

In this and the following table O.Fl. stands for oxidizing flame, and R.Fl. for phates, after treating with R.Fl. on charcoal, is detected by pressing the sub-alkaline substance.

	ALONE ON THE CHARCOAL AND IN THE FORCEPS.	WITH BORAX ON A PLATINUM WIRE.
Baryta BaO.	The hydrate fuses, boils, swells, becomes fixed on the surface and then sinks into the coal with violent ebullition. The carbonate fuses to a clear bead easily, and becomes enamel white on cooling. On repeated fusing it becomes caustic (alkaline) and is absorbed. Colors the flame yellowish green.	The carbonate dissolves to a clear bead, with effervescence, and can be flamed enamel white with a certain amount; with more it becomes enamel-white of itself on cooling.
Strontia, SrO.	The hydrate behaves like Baryta. The carbonate fuses only on the edges, ramifying like cauliflower; the projections are luminous, tinge the R.Fl. red, and have an alkaline reaction. In the forceps, colors the flame crimson.	Like Baryta.
Lime, CaO.	CaO. is unaltered. CaCO ₃ becomes caustic, whiter, more luminous, then alkaline, and crumbles to a powder if moistened. In forceps, colors flame feebly red.	Dissolves easily. The clear bead can be flamed opaque. CaCO ₃ dissolves with effervescence. With excess, the bead becomes cloudy and crystalline on cooling, but never so milk-white as with Baryta and Strontia.
Magnesia, MgO.	Magnesia is infusible, and unaltered. The carbonate is very luminous when heated, is decomposed and becomes strongly alkaline.	Like Lime but not so strongly crystalline.

TABLE V.

with reagents before the blowpipe.

reducing flame. The alkaline property of the earths their carbonates and substance on moistened tumeric paper, which becomes brown by the action of the

WITH MICROCOSMIC SALT ON A PLATINUM WIRE.	WITH Na_2CO_3 ON CHAR- COAL.	
As with Borax.	Fuses with it and is absorbed by the charcoal.	
Like Baryta.	SrO is insoluble. SrCO_3 fuses with any great amount of Na_2CO_3 to a clear bead, milk-white on cooling. More strongly heated, the bead boils and the caustic earth is absorbed. If more is added it does not dissolve, but becomes caustic and goes into the coal.	
Dissolves largely (the carbonate with effervescence) to a clear bead that can be flamed opaque when rather saturated. Perfectly saturated, the bead becomes milk-white on cooling.	Insoluble. The soda goes into the coal leaving the lime behind.	
		WITH SOLUTION OF Co_2NO_3 .
Like Lime.	Like Lime.	After long blowing has a pale flesh color, only properly seen when quite cold. Phosphate and Arsenate fuse and become quite red.

TABLE, VI.

Behavior of the more important metallic oxides, alone and with

In using BUNSEN'S FLAME METHOD the assay is supported on a carbonized Bunsen gas flame: the reactions may consist in reduction of the oxide to metal and held so as to cut the portion of the flame charged with the metallic flame; or of metallic globules (or grains) on the support.

In this table O.Fl. signifies Oxidiz.

IN THE OXIDIZING AND		
METALLIC OXIDES.	ALONE ON CHARCOAL, ETC.	WITH BORAX ON PLATINUM WIRE.
Antimony.	O.Fl. Gives off dense fumes which form white coating on the charcoal. R.Fl. is reduced and volatilized, coating the coal with Sb_2O_3 ; tinges the flame greenish-blue.	O.Fl. Dissolves largely to a clear bead (yellowish (h.)), colorless (c.). <i>On coal</i> the dissolved oxide can be driven off. R.Fl. The bead treated only for a short time in O.Fl. becomes on charcoal grayish and clouded from reduced antimony; but with prolonged blowing this volatilizes, leaving a clear bead. With Tin the bead becomes gray or black according to the degree of saturation.
Arsenic.	Volatilizes below a red heat, giving dense white fumes.	o.
Bismuth.	When lightly touched with O. Fl. it becomes yellow, then easily melts to a brown mass, pale yellow (c.). It is easily reduced on coal in either O.Fl. or R.Fl. to a brittle metallic globule, volatilizable in either flame without coloring the flame, but forming a coating of yellow oxide (h.); beyond this coating is another thin one of white carbonate.	O.Fl. Dissolves easily to a clear yellow bead, colorless (c.), if a little oxide is used. With more oxide the bead is yellowish-red (h.), yellow on cooling and opalescent (c.). R.Fl. The bead on coal is at first gray and clouded, then the oxide is reduced to a metal with effervescence, and the bead becomes clear. Addition of Tin accelerates the reduction.

TABLE VI.

reagents, on charcoal, in the gas flame, and before the blowpipe.
 match, or on a thread of Asbestos, and held in the upper part of the colorless tallic vapor which may be condensed on a porcelain crucible filled with cold vapor, forming characteristic stains on the porcelain; formation of colored

ing Flame; R.Fl., Reducing Flame.

REDUCING FLAMES.

BUNSEN'S FLAME METHOD.	WITH CARBONATE OF SODA, (AND OTHER REAGENTS.)	With $\text{Na}_2\text{S}_2\text{O}_3$, heated in a test tube give colored mass.
Reduced to brittle globules, giving off greenish - blue flame: the vapor cut by cold porcelain surface gives black velvet coating of Sb. insoluble in NaClO .	Is reduced very easily on coal in either flame, but the metal volatilizes very rapidly, coating the coal with a white oxide of Antimony.	Red.
Bluish flame with dense white smoke: vapor cut by cold porcelain surface gives lustrous brown coating, soluble in NaClO .	Is reduced on charcoal with evolution of arsenical fumes (odor of garlic).	Yellow
Easily reduced to brittle globules; does not color flame: vapor cut by cold porcelain surface deposits a grayish-brown lustrous coating.	On charcoal is reduced immediately to metallic Bismuth, giving a very fusible and brittle globule. Any compound of Bismuth heated on coal, in O.Fl., with equal parts of KI, and S. gives a scarlet coating on the coal, of BiSI .	Black.

TABLE VI.—

METALLIC OXIDES.	ALONE ON CHARCOAL, ETC.	WITH BORAX ON PLATINUM WIRE.
Cadmium.	O.Fl. On Pt. foil unchanged. R.Fl. On charcoal it shortly disappears giving off brown fumes, and coats the surrounding coal with reddish brown to dark yellow powder, the color of which is properly seen only when cold. The coal beyond the coating shows a variegated tarnish.	O.Fl. Dissolves very largely to a clear yellowish bead, almost colorless (c.). When strongly saturated, the bead becomes milk-white by flaming, and with still more becomes enamel-white of itself on cooling. R.Fl. The bead containing the oxide boils on coal: the Cadmium is reduced and immediately volatilized, coating the coal with dark yellow oxide.
Chromium.	Unaltered in O.Fl. and R.Fl.	O.Fl. Dissolves slowly but colors strongly. With little oxide the bead appears yellow (h.) but yellowish-green (c.) With more oxide it is dark red (h.), but becomes yellow on cooling, and fine yellowish-green (c.). R.Fl. The slightly saturated bead is green (h. and c.). With more it becomes emerald-green. Tin causes no change.
Cobalt.	O.Fl. Unchanged. R.Fl. Shrinks somewhat and is reduced without fusing to a metal (magnetic) and assumes a metallic lustre when rubbed in a mortar.	O.Fl. Colors very strongly; the bead is pure smalt-blue (h. and c.). The strongly saturated bead is so dark-blue as to appear black, but the blue color may be seen by melting the bead and drawing it out into a thread. R.Fl. As in O.Fl.
Copper.	O.Fl. Fuses to a black globule which soon spreads out and is reduced to metallic copper on the lower side. R.Fl. Reduced below the melting point of copper; the reduced particles show a copper lustre, but when the blast is stopped, oxidize again on the surface, becoming black or brown. Strongly heated, it fuses to a globule of copper.	O.Fl. Colors rather strongly; a little causes a green bead (h.), blue (c.). With more it is a bark green to opaque (h.), greenish-blue (c.) R.Fl. Saturated to a certain degree the bead becomes colorless (h.), but red and opaque (c.), (cuprous oxide). On coal the oxide is reduced to a metal and the cold bead is colorless. A bead containing oxide treated on coal with Tin becomes brownish-red and opaque on cooling.
Gold.	Is reduced on ignition in either flame, and can easily be melted to a globule.	O.Fl. Reduced without dissolving. On coal can be fused to a button. R.Fl. The same.

CONTINUED.

BUNSEN'S FLAME METHOD.	WITH CARBONATE OF SODA, (AND OTHER REAGENTS.)	WITH $\text{Na}_2\text{S}_2\text{O}_3$.
No globule, orange flame and reddish smoke: the vapor cut by cold porcelain surface gives a coating from brown to blue-black, according to depth of coating.	O.Fl. Insoluble. R.Fl. On coal immediately reduced and volatilized, coating coal with reddish brown to dark yellow oxide. The more remote portions of the coal assume a variegated tarnish.	Yellow.
o.	O. Fl. On Pt. wire dissolves to a dark brownish-yellow bead, opaque yellow on cooling. R.Fl. The bead is opaque and green on cooling; cannot be reduced to a metal on charcoal but remains as green Cr_2O_3 while the soda is absorbed by the coal.	Green.
Infusible Magnetic powder.	O.Fl. On Pt. wire, in very small quantity, dissolves to to a transparent, feebly-red bead, gray when cold. R.Fl. On coal is reduced to a gray magnetic powder, assuming a metallic lustre by friction.	Black.
Green flame but no coating by condensing vapor; fuses to brown globules which show copper color by flattening and rubbing with a knife-blade on a slip of glass.	O.Fl. Dissolves on Pt. wire to a green bead (h.), losing color and becoming opaque on cooling. R.Fl. On coal is reduced very easily to a metal, which can be fused to one or more globules by sufficient heat.	Black.
Purple stain with small amount, but with larger amount yellow globules very malleable, insoluble in HNO_3 .	As with Borax. The soda goes into the coal.	Black.

TABLE VI.—

METALLIC OXIDES.	ALONE ON CHARCOAL, ETC.	WITH BORAX ON PLATINUM WIRE.
Iron.	O.Fl. Unchanged. R.Fl. Becomes black and magnetic (Fe_3O_4)=Magnetic oxide.	O.Fl. With little oxide the bead is yellow (h.), colorless (c.); with more it is red (h.), yellow (c.); with still more, dark-red (h.), and dark-yellow (c.) R.Fl. The bead becomes bottle-green. On coal with Tin it becomes at first bottle-green (Fe_3O_4), but on longer blowing, vitrol-green (FeO).
Lead.	Minium heated on Pt. foil blackens, and heated to incipient redness, changes to yellow oxide. At a higher temperature this oxide fuses to a yellow bead. On coal the oxide of lead is reduced by either flame with effervescence, and the metal gradually volatilizes, coating the coal with yellow oxide; beyond this is another thinner coat of white carbonate. The coats disappear under the R.Fl., tinging the flame azure-blue.	O.Fl. Dissolves easily to a clear yellow bead, colorless (c.), and which with a larger quantity, becomes opaque by flaming; with still more it becomes opaque and enamel-yellow of itself on cooling. R.Fl. The bead spreads out on coal, and becomes cloudy: on continuing the blast, the oxide reduces with effervescence to a metal, and the bead becomes clear again.
Manganese.	O.Fl. Infusible. In a hot enough flame both the dioxide and sesquioxide are changed to proto-sesquioxide, yielding O_2 , and turning brown-red. R.Fl. The same.	O.Fl. colors very intensely. The hot bead is violet but on cooling is a violet-red. An excess renders the bead quite black and opaque, the color being made visible by drawing the fused bead out into a thread. R.Fl. The bead becomes colorless (protoxide.) With a very dark bead this succeeds better on coal and with Tin.
Mercury.	Is instantly reduced and volatilized, giving a gray tarnish of Hg. on the coal some distance from the assay.	o.

CONTINUED.

BUNSEN'S FLAME METHOD.	WITH CARBONATE OF SODA, (AND OTHER REAGENTS.)	WITH $\text{Na}_2\text{S}_2\text{O}_8$.
Infusible magnetic grains.	O.Fl. Insoluble. R.Fl. It is reduced on coal, yielding a gray, magnetic, metallic powder, when the particles of coal are washed away.	Black.
Colors flame sky-blue; forms metallic globules: vapor cut with cold porcelain surface gives a brown coating of the metal.	O.Fl. On Pt. wire it dissolves easily to a clear bead, becoming yellowish and opaque on cooling. R.Fl. Is immediately reduced on coal to a metal, which afterwards coats the coal with oxide.	Black.
o.	O.Fl. On Pt. foil a very trifling quantity dissolves to a clear, transparent green mass (h.), becoming opaque and bluish green (c.) Addition of KNO_3 assists the coloration. R.Fl. Not reducible to a metal on coal; the soda sinks into the coal, leaving the protoxide behind. Any compound of Mn. fused with KClO_3 on Pt. foil gives a purple mass when cold.	Green.
Volatilized easily, gives a gray stain to cold porcelain surface of Hg., which may be united into a globule.	Heated to redness in closed tube it is reduced and vaporized, the vapors condense on sides of tube as a gray film, which may be united into a globule by rubbing with a glass rod.	Black.

TABLE VI.—

METALLIC OXIDES.	ALONE ON CHARCOAL, ETC.	WITH BORAX ON PLATINUM WIRE.
Molybdic Oxide.	<p>O.Fl. Fuses, spreads out, volatilizes, and forms, at a certain distance, a yellow pulverulent coat, consisting of small crystals near the assay. The coat becomes white on cooling and the crystals colorless. Beyond this coat is a thinner non volatile film MoO_3, dark copper-color (c.) and of metallic lustre.</p> <p>R.Fl. The greater part sinks into the coal, and by a good flame can be reduced to a metal, which is obtained as a gray powder after washing away the coal.</p>	<p>O.Fl. Dissolves easily and largely to a clear bead, yellow (h.), colorless (c.). A very large addition produces a bead dark yellow to dark red (h.), and opaline to a bluish-gray enamel (c.)</p> <p>R.Fl. The bead produced in O. Fl. becomes brown with a certain degree of saturation, and still more, is opaque (MoO_3). In good flame black flocks of MoO_3, separate and can be very distinctively seen in the yellowish bead when it is pinched out flat.</p>
Nickel.	<p>O.Fl. Unchanged.</p> <p>R.Fl. On coal is reduced to a metallic, coherent and infusible powder, which by friction in the mortar assumes a metallic lustre, and is decidedly magnetic.</p>	<p>O.Fl. Colors quite intensely; a little colors the hot bead violet, but a pale reddish brown (c.); with more the colors are darker.</p> <p>R.Fl. The bead becomes gray and cloudy, or quite opaque, owing to finely divided metallic Nickel. On continuing the blast the metallic particles collect together without fusing, and the bead becomes colorless. On coal especially with Tin the reduction is more rapid and the Nickel unites with the Tin to form a globule.</p>
Silver.	<p>Reduced easily to metallic Silver in either flame; readily fuses to one or more globules.</p>	<p>O.Fl. Partly dissolved and partly reduced, the cold bead is opalescent or milk-white, according to the amount dissolved.</p> <p>R.Fl. On coal the bead is first grayish from reduced Silver, but after all the Silver is separated and fused to a globule the bead becomes clear and colorless.</p>

CONTINUED.

BUNSEN'S FLAME METHOD.	WITH CARBONATE OF SODA, (AND OTHER REAGENTS.)	WITH $\text{Na}_2\text{S}_2\text{O}_3$.
Colors flame greenish yellow; the vapor cut by cold porcelain surface gives a stain from purplish brown to deep blue.	O.Fl. On Pt. wire fuses with effervescence to a clear bead milk white on cooling. R.Fl. On coal fuses with effervescence at first, but afterwards the fused mass is absorbed by the coal, and the greater part of the acid is reduced to metallic Molybdenum, which can be obtained as a steel gray powder by washing away the particles of coal.	Brown.
Magnetic grains.	O.Fl. Insoluble. R.Fl. On coal is easily reduced to white metallic particles, which after the coal is washed away, follow the magnet readily.	Black.
Easily reduced to white globules, very malleable.	Is instantly reduced to one or more globules of Silver, while the soda sinks into the coal.	Black.

TABLE VI.—

METALLIC OXIDES.	ALONE ON CHARCOAL, ETC.	WITH BORAX ON PLATINUM WIRE.
Tin.	<p>O.Fl. The oxide becomes strongly luminous, and is yellow while hot, but dirty yellowish white when cold.</p> <p>R.Fl. Is reduced to a metal by a <i>continued and strong flame</i>; a trifling coating of SnO_2 being generally formed near the assay.</p>	<p>O.Fl. Dissolves in trifling quantity, and very slowly to a clear bead, remaining colorless on cooling and not becoming opaque by flaming. A saturated and perfectly cold bead, when heated to low redness, becomes opaque, loses its spherical shape, and shows distinct crystallization.</p> <p>R.Fl. A not saturated bead is unchanged. On coal some Tin can be reduced from a bead containing much oxide.</p>
Zinc.	<p>O.Fl. Becomes transiently yellow, is infusible, but strongly luminous when ignited.</p> <p>R.Fl. Gradually disappears, being reduced, volatilized, and again oxidized and forms a new coating on another part of the coal, yellow (h.) white (c.)</p>	<p>O.Fl. Dissolves easily and largely to a clear bead, yellowish (h.) colorless (c.). With more oxide the bead becomes enamel-white by flaming; with still more the bead becomes enamel-white of itself on cooling.</p> <p>R.Fl. The saturated bead becomes cloudy and grayish by the first blast, but after longer blowing is clear again. On coal, is gradually reduced, volatilized and re-oxidized, forming a coating on the coal.</p>

CONTINUED.

BUNSEN'S FLAME METHOD.	WITH CARBONATE OF SODA, (AND OTHER REAGENTS.)	WITH $\text{Na}_2\text{S}_2\text{O}_3$.
The Chlorides of Tin yield a vapor which deposits a brown metallic stain on cold porcelain, or a chalky coating of Stannic oxide.	O.Fl. On Pt. wire combines with the Soda with effervescence to a swollen infusible mass. R.Fl. Reduced to Tin on coal. By using KCy. the metal can be reduced more easily and effectually than with Na_2CO_3 .	Brown.
Zinc compounds strongly heated give a vapor which deposits a brown metallic stain on cold porcelain surface.	O.Fl. Insoluble. R.Fl. On coal is reduced, volatilized and re-oxidized, giving a Zinc coating. With a good flame the Zinc flame may even be produced.	White.

DETERMINATION OF ACIDS BY BLOWPIPE.

The bases having been found during the examination of the substance by the preceding pages, the next step is the determination of the acid present. A small quantity of the finely powdered substance is placed in a clean test tube and treated according to the following table.

SALTS.	HEATED WITH KHSO_4 AND MnO_2 .	MOISTEN'D WITH DILUTE HCl . AND HEATED.	OTHER REACTIONS.
Acetates.	Evolve odor of Vinegar.	o.	o.
Borates.	o.	The moistened mass pressed on Turmeric paper gives red brown stain.	Moistened with H_2SO_4 and heated in colorless gas flame give green flame.
Bromides.	Evolve red-brown vapors of Bromine.	o.	The vapors of Bromine condense in drops on sides of tube. Stain the skin bright yellow.
Carbonates.	Effervesce. CO_2 evolved. Test by lime water.	Brisk effervescence. CO_2 evolved. Test by lime water.	A borax bead dipped in a carbonate and heated slightly effervesces—plunge the bead into a solution of lime water white precipitate, CaCO_3 .
Chlorates.	Give off O . Test by spark on splinter.	Evolve Oxides of Cl .	Heated alone in a tube evolve O gas and are converted into Chlorides. Test the residue for Cl .
Chlorides.	Evolve Cl . color and odor.	o.	Bead of microcosmic salt saturated with CnO , dipped in a Chloride and heated in oxidizing flame gives flame of CuCl_2 —blue.
Cyanides.	Evolve HCy . odor.	o.	Most Cyanides give the flame a peach-blossom tint.
Fluorides.	Evolve HF .	o.	HF gas evolved; etches sides of test tube.
Iodides.	Evolve violet vapors.	o.	Vapors of Iodine condense into dark colored scales on sides of tube.
Nitrates.	Evolve red vapors which do not condense.	o.	Nitrates heated on coal deflagrate.

DETERMINATION OF ACIDS BY BLOWPIPE.—CONTINUED.

SALTS.	HEATED WITH KHSO_4 AND MnO_2 .	MOISTEN'D WITH DILUTE HCl AND HEATED.	OTHER REACTIONS.
Phosphates.	o.	o.	Heated strongly in a tube with small piece of mg. wire are decomposed, forming Phosphide of Mg. The cooled mass moistened with water and heated gently evolves PH_3 .
Sulphates.	o.	o.	Fused with Na_2CO_3 on coal gives dark colored mass. The mass placed on silver plate and moistened stains silver brown to black.
Sulphides.	Evolve H_2S . Blackens lead paper. Offensive odor.	Evolve H_2S . Blackens lead paper. Offensive odor.	Most Sulphides heated with Na_2CO_3 in a tube give a mass which will stain moistened silver plate brown to black.
Sulphites.	Evolve SO_2 . Odor of burning match.	Evolve SO_2 . Odor of burning match.	Heated with Na_2CO_3 in a tube give a mass which will blacken moistened silver plate.
Silicates.	o.	Soluble Silicates precipitate gelatinous Silica on long boiling	Undissolved skeleton of Silica in microcosmic salt bead (see page 14).

LIST OF THE ELEMENTS, SYMBOLS, ATOMICITIES, AND COMBINING WEIGHTS.

NAME.	SYMBOL.	ATOMICITY.	COMBINING WEIGHTS.
Aluminum	Al.	III and VI	27.4
Antimony	Sb.	III and V	122.
Arsenic	As.	III and V	75.
Barium	Ba.	II	137.
Beryllium	Be.	II	9.
Bismuth	Bi.	III and V	210.
Boron	B.	III	11.
Bromine	Br.	I	80.
Cadmium	Cd.	II	112.
Cæsium	Cs.	I	133.
Calcium	Ca.	II	40.
Carbon	C.	IV	12.
Chlorine	Cl.	I	35.5
Cerium	Ce.	IV	92.
Chromium	Cr.	III	52.2
Cobalt	Co.	II	58.8
Copper	Cu.	II	63.
Didymium	D.	II	95.
Erbium	E.	II	112.6
Fluorine	F.	I	19.
Gallium	Ga.	III	69.8
Gold	Au.	III	197.
Hydrogen	H.	I	1.
Indium	In.	III	113.4
Iodine	I.	I	127.
Iridium	Ir.	II	198.
Iron	Fe.	II and VI	56.
Lanthanum	La.	II	93.6
Lead	Pb.	II	207.
Lithium	Li.	I	7.
Magnesium	Mg.	II	24.
Manganese	Mn.	II	55.
Mercury	Hg.	II	200.
Molybdenum	Mo.	III	96.
Nickel	Ni.	II	58.8
Niobium	Nb.	V	94.
Nitrogen	N.	III and V	14.
Osmium	Os.	VI	199.2
Oxygen	O.	II	16.
Palladium	Pd.	II	106.
Phosphorus	P.	III and V	31.
Platinum	Pt.	II	197.5
Potassium	K.	I	39.1
Rhodium	Rh.	II	104.4
Rubidium	Rb.	I	85.4
Ruthenium	Ru.	VI	104.4
Selenium	Se.	VI	79.5

LIST OF THE ELEMENTS, SYMBOLS, ETC.—CONTINUED.

NAME.	SYMBOL.	ATOMICITY.	COMBIN NG WEIGHTS.
Silver	Ag.	I	108.
Silicon	Si.	I V	28.
Sodium	Na.	I	23.
Strontium	Sr.	II	87.5
Sulphur	S.	V I	32.
Tantalum	Ta.	V	182.
Tellurium	Te.	V I	128.
Thallium	Tl.	III	204.
Thorium	Th.	II	231.5
Tin	Sn.	II and IV	118.
Titanium	Ti.	I V	50.
Tungsten	W.	V I	184.
Uranium	U.	II	120.
Vanadium	V.	V	51.2
Yttrium	Y.	II	93.
Zinc	Zn.	II	65.
Zirconium	Zr.	I V	90.

SOLUTION.

After the preliminary examination of a solid, the next step in analysis is to bring it into a liquid form, or dissolve it. In a complex body, a partial separation of its components may often be effected in the act of solution, and valuable hints in regard to the nature of a substance may be derived from its behavior with different solvents. Thus, one part of the substance may be soluble in water, while another is insoluble in water but soluble in acids, while another part is insoluble in water and acids. By dissolving in water and removing in this form, we may entirely separate this part of the substance from the rest; by treating the residue with acids, we may separate the two remaining classes of bodies in the substance. An important step in analysis may thus be secured in the act of solution.

THE SUBSTANCE IS NOT METALLIC. Non-metallic substances may be divided into three classes, according to their respective behavior with water and acids. These classes are:

- 1°. Substances soluble in water.
- 2°. Substances insoluble (or sparingly soluble) in water, but soluble in Nitric Hydrochloric or Nitro-Hydrochloric acids.
- 3°. Substances insoluble in water and in any of these acids.

Reduce the substance to a fine powder in a porcelain mortar; place 10 grains of the powder in a test tube, add 20 volumes of distilled water and heat to boiling.

Soluble in water. If the substance entirely dissolves it belongs to the first class. If it does not appear to dissolve even after protracted boiling, let the solid matter settle, pour off a little of the clear liquid and evaporate on a clean slip of Platinum foil or of glass; if nothing remains, or only a very slight stain, the substance is practically insoluble in water, but if a distinct residue remains the substance is partially soluble in water; in which case, boil the undissolved residue with more water till no more will dissolve, and mix all the watery solutions for analysis. If the water will dissolve only a part of the substance, the original substance probably contains at least two bodies of different solubilities, which should be analyzed separately.

2. *Insoluble in water, but soluble in acids.* Treat the residue which water will not dissolve, with dilute Hydrochloric acid. If it does not dissolve heat to boiling; if this fails to effect complete solution, decant the clear fluid into another test tube and boil the residue with concentrated Hydrochloric acid; if it dissolves, add it to the fluid in the other test tube for analysis.

The reactions which may manifest themselves in this operation ought to be carefully watched; they may be, 1. Effervescence from the presence of Carbonates, Sulphites, Sulphides or Cyanides; 2. Evolution of Chlorine or its oxides, from presence of Peroxides, Chromates, etc.; 3. Odor of Hydrocyanic Acid from presence of insoluble Cyanides.

If the substance is not entirely dissolved (except separated Sulphur or gelatinous Silica) set aside this test tube with its contents, and treat some of the original substance with Nitric Acid and heat to boiling; if red fumes escape, it indicates an oxidizing process. If the substance does not dissolve (except Sul-

phur or Silica,) mingle the contents of the test tubes in which the substance has been boiled in HCl, and HNO_3 , and ascertain if the Nitro-Hydrochloric acid thus formed will dissolve it; if necessary, heat to boiling. The substance, or that portion of the substance which dissolves in acids, belongs to the second class—*Substances insoluble in water, but soluble in acids.*

8. *Insoluble substances.* The substances which remain insoluble after this successive treatment with water and acids, belongs to the third class—*Substances insoluble or very sparingly soluble in water and in acids.*

The bodies included in this class are Sulphates of Barium, Strontium, Calcium, and Lead; the Chlorides, Bromides, Iodides, Ferrocyanides, and Ferricyanides of Silver; the Ferrocyanides and Ferricyanides of several other metals; Silica and many Silicates; Native Alumina and Alumina which has been ignited, and many Aluminates; ignited Chromic oxide and Chrome iron ore; ignited and native oxide of Tin.; some Metaphosphates and some Arsenates; Fluoride of Calcium and a few other compounds of Fluorine; Sulphur and Carbon.

The preliminary examination by Table I. will give valuable information in regard to the composition of these insoluble compounds. If from such examination, it becomes probable that the substance belongs to any of the following classes, the special treatment of that class may be instituted at once. But if no indication of this nature appears, the finely powder substance is intimately mixed with 4 parts of Na_2CO_3 and converted into a soluble form by fusing on Platinum foil or in a Platinum crucible (Platinum vessels should never be used with compounds of As, Sb, Sn, Pb, Bi, or any easily reducible metal, because fusible alloys of Platinum may be formed and the vessel perforated). The fused mass is boiled with ten volumes of distilled water, the watery solution (which will contain an excess of Na_2CO_3) is filtered off and preserved for detecting the acid radical; the thoroughly washed residue is dissolved in HCl, or HNO_3 , and analyzed for the basic substance.

SULPHATES with Na_2CO_3 upon charcoal in R. Fl. give a hepar, i. e., the moistened mass pressed upon Silver foil or Lead paper gives a brownish stain—Sulphate of Lead with Na_2CO_3 in R. Fl. on charcoal gives a metallic globule; it is blackened by NH_4HS , and is soluble in basic Tartrate of Ammonium. Sulphate of Calcium is somewhat soluble in water, and its solubility is increased by Conc. HCl.

SILICA AND SILICATES, with Microcosmic Salt give a skeleton of Silica. Treated with Na_2CO_3 , the Silica becomes soluble in water; when treated with HCl, the Silica may separate as a gelatinous mass, or, if the watery solution is acidified and evaporated to dryness, the Silica is left in an insoluble form.

FLUORIDE OF CALCIUM AND INSOLUBLE FLUORIDES. With concentrated H_2SO_4 give off gaseous HF = which etches glass. Powder the material and mix it with a little finely powdered sand or glass, place it in a watch glass, and moisten with Conc. H_2SO_4 , and warm gently; if white vapors are given off which redden blue litmus paper, a Fluoride is probably present.

CHLORIDE, BROMIDE, AND IODIDE OF SILVER. Blackened by NH_4HS . If fused with Na_2CO_3 , the Silver is left in the form of carbonate, readily soluble

in HNO_3 . If any compound of Silver is treated with Na_2CO_3 on charcoal in R. Fl. a globule of Silver is obtained.

OXIDE OF TIN. *With Na_2CO_3 and KCy , on Charcoal in R. Fl. affords a metallic globule; The Oxide is blackened by NH_4HS .* After fusing with Na_2CO_3 the oxide is soluble in HCl .

ALUMINA AND ALUMINATES. *When moistened with a solution of Co_2NO_3 and then ignited they give a blue infusible mass.* They all are rendered soluble by fusing with four parts of KHSO_4 ; then treated with water or dilute HCl .

COMPOUNDS OF CHROMIUM. With Borax these give a green bead both in O. Fl. and R. Fl. They are rendered soluble by fusing with KHSO_4 , or KNO_3 . Chrome iron ore requires successive treatment by both methods.

CARBON is usually black; is insoluble in water and in all acids; if treated with fused KNO_3 , it burns vividly and K_2CO_3 is formed; if placed on Platinum foil, and the foil is intensely heated by the blow-pipe flame playing on the under side of the foil, the carbon is always consumed.

INSOLUBLE FERROCYANIDES AND FERRICYANIDES are easily decomposed by boiling for a few minutes in a solution of Na_2CO_3 , when a soluble Ferrocyanide or Ferricyanide of Sodium is formed, and the base is left as a metallic oxide or oxide or carbonate—soluble in dilute acid.

Many other substances insoluble in water and acids, are decomposed by prolonged boiling with alkaline carbonates.

SOLUTION OF SUBSTANCES WHICH ARE METALS OR ALLOYS.

The metals are classified according to their respective behaviour with Nitric Acid.

- I. Metals not acted on by HNO_3 , Gold, Platinum, Iridium and Aluminum.
- II. Metals which are oxidized by HNO_3 , but whose oxides do not dissolve in an excess of this acid or in water: Antimony and Tin.
- III. Metals which are converted into Nitrates, soluble in an excess of the acid or in water: All other metals.

Pour diluted HNO_3 over a small portion of the metal or alloy and apply heat.

1. Complete solution takes place speedily or upon the addition of water; absence of Gold, Platinum, Iridium, Aluminum, Antimony and Tin.
2. A residue is left. If this is metallic, pour off the acid and test the solution to see if any part is soluble in HNO_3 ; wash the residue and pour over it a little HCl ; if it dissolves with brisk effervescence, probable presence of Aluminum; if HCl does not act on the substance, add HNO_3 (thus forming Nitro-Hydrochloric Acid) and dissolve the substance by application of a gentle heat, and examine the solution for Gold, Platinum and Iridium.

If the residue is not metallic but is a white pulverulent substance, it indicates the presence of Antimony or Tin. Pour off the Nitric Acid, wash the residue with water, dissolve it in HCl and examine this solution for Antimony and Tin.

METHOD OF ANALYSIS OF SUBSTANCES IN SOLUTION.

When we have a solution of unknown substances, the first step in its analysis is to separate it into *groups of chemically similar substances by means of the group reagents* HCl , H_2S , NH_4HS , and $(\text{NH}_4)_2\text{CO}_3$ in the presence of NH_4Cl .

Suppose we have a solution containing members of all the groups; if we add to this HCl , to distinct acid reaction, all the Silver and Mercurous bases present will be precipitated as Chlorides, because they are insoluble in water and in HCl . If Lead is present in considerable quantity, the larger part will be precipitated because PbCl_2 is only sparingly soluble in cold water, but a small part will remain in solution because of this sparing solubility. By means of HCl we thus remove all the Silver and Mercurous bases from the solution, and these bases need only be sought in the precipitate thrown down by HCl . If no precipitate form with HCl , these bases are entirely absent. But if HCl is added in quantity insufficient to completely precipitate these bases, the subsequent addition of H_2S will precipitate them as Sulphides, and they will then appear among the members of the second group. The same fact is seen in nearly all the group-reagents; if any group-reagent is used in amount insufficient to produce complete precipitation, the addition of the next group-reagent will precipitate the members of the preceeding groups.* Hence the following rule: *Wherever any group-reagent produces a precipitate, continue to add it till no more precipitate forms.*

In using liquid reagents, it is not advisable to pour into the solution a large quantity of the reagent at once, because many reactions will escape notice. It is best to add the reagents drop by drop, and to observe closely any changes caused by the reagents in the solution for analysis.

Table VII exhibits a scheme for separating unknown substances into groups of chemically similar substances preparatory to final analysis. The group-reagent is added till complete precipitation is secured, and then the entire contents of the test tube are thrown upon a filter to separate the solid part (*precipitate*) from the liquid part which runs through the filter (*filtrate*). The precipitate on the filter is washed with distilled water to remove any adhering portions of the liquid which may contain matters foreign to the precipitate, and this washed precipitate is then dissolved, and special reagents used for its analysis according to the Tables for analysis of the several groups.

The *filtrate* (the clear liquid which passes through the filter) in each case is used for the separation of the succeeding group by use of the next group-reagent. In using the several group-reagents we need to attentively consider the character of the reactions which take place. For example: When we use HCl for precipitating the members of Group I, we expect a white, rapidly-sub-siding precipitate which does not disappear on adding more of the acid. If however we find a gelatinous precipitate, or a milky-white one that long remains in suspension, or the precipitate at first formed seems to diminish on add

*The principal exception is that NH_4HS will dissolve the Sulphides of As., Sb., Sn., Pt. and Au.

ing more of the acid, we suspect the precipitate contains some substance not a member of Group I.

Especial care is required in the use of H_2S , because the solution of this gas, as ordinarily used, is a weak acid by reason of the sparing solubility of the gas. We can never be certain that we have secured the full action of this acid unless the solution smells distinctly of the acid, even after violent shaking of the test tube and its contents.

Wherever we have a solution containing an unknown number of unknown substances, the method of separation by group-reagents and the analysis of each group by itself is indispensable for accurate analysis. But if for any reason we know that we have only the members of one group present, the use of group-reagents is only necessary to identify the group, and instead of separating the group-precipitate and dissolving this for analysis, we may use the original solution at once for the application of the special reagents which serve to identify the members of that group. This method is specially applicable in laboratory practice where the student is set to analyze single salts. In the absence of such information it is best to follow the regular method, or at least to use the group-reagents in such way as to show the absence of other groups before using the original solution with the special reagents to identify the members of any group. Care and forethought may thus shorten many analytical processes without thereby impairing the accuracy of the results. In this study heedless haste and slovenly manipulation mature an early harvest of error and disappointment.

TABLE VII.

For classifying bases into groups by precipitation with the four in succession; the *Filtrate* (after separation of the precipitate) group.

To the substance in solution add HCl. to acid reaction: if a precipitate forms which is GROUP I.

<p align="center">GROUP I.</p> <p>The precipitate by HCl. may contain: $\left. \begin{array}{l} \text{AgCl.} \\ \text{PbCl}_2. \\ \text{Hg}_2\text{Cl}_2. \end{array} \right\}$ White. Analyze by Table VIII.</p> <hr/> <p>A precipitate may form of S. (milky white) from alkaline Polysulphides, insoluble in HCl—of H_2SiO_3. (white and gelatinous) from Alkaline Silicates, insoluble in HCl. soluble in KHO.— of $\left. \begin{array}{l} \text{BiOCl.} \\ \text{SbOCl.} \end{array} \right\}$ White. Soluble in excess of HCl.</p>	<p>To the filtrate from which HCl. will not form a pre-thoroughly. The precipitate is GROUP II.</p> <hr/> <table border="1"> <tr> <td data-bbox="411 538 670 972"> <p align="center">GROUP II.</p> <p>The precipitate by H_2S. may contain</p> $\left. \begin{array}{l} \text{PbS.} \\ \text{CuS.} \\ \text{HgS.} \\ \text{Bi}_2\text{S}_3. \end{array} \right\}$ Black. $\left. \begin{array}{l} \text{Au}_2\text{S}_3. \\ \text{PtS}_2. \end{array} \right\}$ Brown-black. SnS—Brown. $\left. \begin{array}{l} \text{CdS.} \\ \text{As}_2\text{S}_3. \end{array} \right\}$ Yellow. SnS_2.—Dirty yellow. $\left. \begin{array}{l} \text{Sb}_2\text{S}_3. \\ \text{Sb}_2\text{S}_5. \end{array} \right\}$ Orange. Analyze by Table IX. </td><td data-bbox="670 538 945 972"> <p>To the filtrate from which NH_4HS. to complete</p> <hr/> <p align="center">GROUP III.</p> <p>The precipitate by NH_4HS may contain:</p> $\left. \begin{array}{l} \text{FeS.} \\ \text{CoS.} \\ \text{NiS.} \end{array} \right\}$ Black. MnS. flesh-colored. ZnS. dirty white. $\text{Al}_2(\text{HO})_6$. $\left\{ \begin{array}{l} \text{Gelatinous} \\ \text{white or gr'n-} \\ \text{ish white in} \\ \text{presence of} \\ \text{trace of Iron} \\ \text{Salts.} \end{array} \right.$ $\text{Cr}_2(\text{HO})_6$. $\left\{ \begin{array}{l} \text{Dirty green} \\ \text{or peach blos-} \\ \text{som.} \end{array} \right.$ Analyze by Table X. </td></tr> </table> <hr/> <p>A precipitate may form of S. (milky white) from the presence of a Ferric Salt, or a Chromate.</p>	<p align="center">GROUP II.</p> <p>The precipitate by H_2S. may contain</p> $\left. \begin{array}{l} \text{PbS.} \\ \text{CuS.} \\ \text{HgS.} \\ \text{Bi}_2\text{S}_3. \end{array} \right\}$ Black. $\left. \begin{array}{l} \text{Au}_2\text{S}_3. \\ \text{PtS}_2. \end{array} \right\}$ Brown-black. SnS —Brown. $\left. \begin{array}{l} \text{CdS.} \\ \text{As}_2\text{S}_3. \end{array} \right\}$ Yellow. SnS_2 .—Dirty yellow. $\left. \begin{array}{l} \text{Sb}_2\text{S}_3. \\ \text{Sb}_2\text{S}_5. \end{array} \right\}$ Orange. Analyze by Table IX.	<p>To the filtrate from which NH_4HS. to complete</p> <hr/> <p align="center">GROUP III.</p> <p>The precipitate by NH_4HS may contain:</p> $\left. \begin{array}{l} \text{FeS.} \\ \text{CoS.} \\ \text{NiS.} \end{array} \right\}$ Black. MnS . flesh-colored. ZnS . dirty white. $\text{Al}_2(\text{HO})_6$. $\left\{ \begin{array}{l} \text{Gelatinous} \\ \text{white or gr'n-} \\ \text{ish white in} \\ \text{presence of} \\ \text{trace of Iron} \\ \text{Salts.} \end{array} \right.$ $\text{Cr}_2(\text{HO})_6$. $\left\{ \begin{array}{l} \text{Dirty green} \\ \text{or peach blos-} \\ \text{som.} \end{array} \right.$ Analyze by Table X.
<p align="center">GROUP II.</p> <p>The precipitate by H_2S. may contain</p> $\left. \begin{array}{l} \text{PbS.} \\ \text{CuS.} \\ \text{HgS.} \\ \text{Bi}_2\text{S}_3. \end{array} \right\}$ Black. $\left. \begin{array}{l} \text{Au}_2\text{S}_3. \\ \text{PtS}_2. \end{array} \right\}$ Brown-black. SnS —Brown. $\left. \begin{array}{l} \text{CdS.} \\ \text{As}_2\text{S}_3. \end{array} \right\}$ Yellow. SnS_2 .—Dirty yellow. $\left. \begin{array}{l} \text{Sb}_2\text{S}_3. \\ \text{Sb}_2\text{S}_5. \end{array} \right\}$ Orange. Analyze by Table IX.	<p>To the filtrate from which NH_4HS. to complete</p> <hr/> <p align="center">GROUP III.</p> <p>The precipitate by NH_4HS may contain:</p> $\left. \begin{array}{l} \text{FeS.} \\ \text{CoS.} \\ \text{NiS.} \end{array} \right\}$ Black. MnS . flesh-colored. ZnS . dirty white. $\text{Al}_2(\text{HO})_6$. $\left\{ \begin{array}{l} \text{Gelatinous} \\ \text{white or gr'n-} \\ \text{ish white in} \\ \text{presence of} \\ \text{trace of Iron} \\ \text{Salts.} \end{array} \right.$ $\text{Cr}_2(\text{HO})_6$. $\left\{ \begin{array}{l} \text{Dirty green} \\ \text{or peach blos-} \\ \text{som.} \end{array} \right.$ Analyze by Table X.		
	<p>The precipitate may also contain Phosphates, Arsenates or Oxalates of</p> $\left. \begin{array}{l} \text{White, soluble in} \\ \text{HCl. insoluble in} \end{array} \right\} \left. \begin{array}{l} \text{Al.} \\ \text{Ba.} \\ \text{Sr.} \\ \text{Ca.} \\ \text{Mg.} \end{array} \right.$ KHO . H_2SiO_3 , insoluble in HCl. but soluble in KHO.		

TABLE VII.

GROUP REAGENTS, HCl, H₂S, NH₄HS, and (NH₄)₂CO₃, used.
from each group being used for precipitating the succeeding

continue to add HCl. till no more precipitate forms. Separate this precipitate

precipitate, add H₂S. till the solution smells strongly of this acid, even after shaking

H₂S. will not form a precipitate, add NH₄Cl. NH₄HO. to alkaline reaction, and precipitation. The precipitate is GROUP III.

To the filtrate from which NH₄HS. will not form a precipitate, add (NH₄)₂CO₃. to complete precipitation. The precipitate is GROUP IV.

GROUP IV.	GROUP V.
<p>The precipitate by (NH₄)₂CO₃. may contain:</p> <p> $\left. \begin{array}{l} \text{BaCO}_3. \\ \text{SrCO}_3. \\ \text{CaCO}_3. \end{array} \right\} \begin{array}{l} \text{White, soluble with effe-} \\ \text{vesence in Acetic Acid.} \end{array}$ </p> <p>Analyze by Table XI.</p>	<p>The filtrate from which (NH₄)₂CO₃. will not form a precipitate, may contain the salts of</p> <p> $\left\{ \begin{array}{l} \text{K.} \\ \text{Na.} \\ \text{Li.} \\ \text{Mg.} \\ \text{NH}_4. \end{array} \right.$ </p> <p>in addition to the Salts of Ammonia added as reagents.</p> <p>Analyze by Table XII.</p>

TABLE VIII.

ANALYSIS OF GROUP I.

The white precipitate thrown down by HCl. and insoluble in excess of that acid.

This precipitate may contain

AgCl.	} White.
PbCl ₂ .	
Hg ₂ Cl ₂ .	

Throw the precipitate on a filter and wash it with a *little cold water*. PbCl₂ is sparingly soluble in cold water, but soluble in 20 volumes of boiling water; if too much water is used in washing the precipitate the whole of the Lead salt may be dissolved and washed away. Pour over the washed precipitate on the filter 20 volumes of boiling water, and reserve the filtrate for analysis for Lead. Then pour over the remaining precipitate NH₄HO. which will dissolve AgCl, but will not dissolve (but blacken) Hg₂Cl₂. Preserve the filtrate for analysis for Silver. Dissolve the blackened precipitate remaining on the filter in a little HNO₃. and use this solution for analysis for Mercury.

LEAD. *Analysis of the hot water filtrate.* If much lead is present the filtrate will deposit needle-shaped crystals of PbCl₂ when it cools. To a test tube half full of solution of H₂S. add 3 or 4 drops of the filtrate; a BLACK PRECIPITATE OR BROWN COLOR* of PbS. will be formed. To a test tube half full of the filtrate add a few drops of H₂SO₄. a WHITE INSOLUBLE PRECIPITATE indicates Lead. To another part of the filtrate add a few drops of HNO₃ then a few drops of KHC₂O₄. a YELLOW PRECIPITATE (subsiding after a time if the solution is dilute) indicates Lead.

A few drops of solution of KI. added to solution of any Lead salt will form a YELLOW PRECIPITATE of PbI₂. Any soluble salt of Lead will precipitate PbCO₃ (white lead) by action of Na₂CO₃. If this PbCO₃ be reduced with the blowpipe on charcoal, a malleable globule of Lead will be obtained, and a yellow incrustation on the coal. Lead colors the blowpipe flame sky-blue.

SILVER. *Analysis of the ammonia solution.* To a small portion of this solution add HNO₃ to acid reaction: a WHITE PRECIPITATE INSOLUBLE IN HNO₃ indicates silver. AgCl. spread on paper and exposed to direct sunlight becomes PURPLE TO BLACK by reduction of the Silver salt.

If the ammonia solution contains Silver, drop a small slip of Zinc into the solution and boil till the Silver is all deposited in a mossy coating (gray to dark brown in color) on the Zinc; pour off the water, wash thoroughly with water, remove the Zinc and Silver, pull off the mossy incrustation of Silver and dissolve it in a small quantity of HNO₃. filter from any residue of AgCl. neutralize any excess of acid with Na₂CO₃. and apply to this solution the special tests for Silver.

*One part of lead in 100,000 parts of water will exhibit this brown coloration upon the addition of H₂S. Any salt of lead will be blackened by action of H₂S.

Soluble salts of Silver are precipitated as white Ag_2CO_3 by Na_2CO_3 . From any solution of Silver salt, HCl precipitates the CURDY WHITE, AgCl insoluble in HNO_3 , but readily soluble in NH_4HO . KHCrO_4 a dark red precipitate, Ag_2CrO_4 ; Na_2HPO_4 a yellow precipitate, Ag_3PO_4 .

The salts of Silver are readily blackened by H_2S . Any compound of Silver treated with Na_2CO_3 in the reducing flame on charcoal will form white globule of Silver. Any salt of Silver held on a carbonized match in the reducing Bunsen flame will form white malleable globules of Silver.

MERCURY. *Analysis of the black residue remaining on the filter after the precipitate was treated with NH_4HO .* The black residue is $\text{NH}_2\text{Hg}_2\text{Cl}$. Dissolve this in HNO_3 and a few drops of HCl by aid of heat, by which means the Mercury is changed to HgCl_2 which is soluble, but will give the reactions for *Mercuric* rather than *Mercurous* base. The fact that the original material was precipitated by HCl proves that it was a *Mercurous* salt, because the *Mercuric* compounds are not precipitated by HCl . The special tests for Mercurous salts must be secured by use of the original solution before precipitation by HCl .

If a drop of the solution of the black residue be placed on a clean slip of copper, after remaining a few minutes, washed off, and the spot rubbed with a cloth, a BRIGHT SILVERY SPOT, READILY VOLATILIZING BELOW A RED HEAT, is proof of the presence of Mercury.

Any dry compounds of Mercury heated with Na_2CO_3 to a high temperature in a test tube will deposit GLOBULES OF MERCURY on the cold part of the tube. Any dry compound of Mercury heated red hot with a mixture of air-slaked lime, carbonate of Sodium and Iodide of Potassium, in a test tube, will form a SUBLIMATE, SCARLET TO YELLOW, on the cold part of the tube.

Special reactions for Mercurous salts. The Caustic Alkalies give a black precipitate Hg_2O . H_2S an immediate black precipitate, Hg_2S . KI gives a greenish-yellow precipitate, Hg_2I_2 . KHCrO_4 gives an orange precipitate, Hg_2CrO_4 , reddish in presence of HNO_3 .

TABLE IX.

ANALYSIS OF GROUP II.

Substances not precipitated by HCl. but completely precipitated in presence of HCl. by H_2S in form of Sulphides.

Some hints concerning the kind of substances present may be derived from the color of the precipitated Sulphides. If it is bright yellow, Arsenic or Cadmium is probably present: if a dirty yellow, Stannic Sulphide: if orange, Antimony: if brown, Stannous Sulphide. If the precipitate is light colored, Lead, Copper, Mercury and Bismuth are all absent, because the Sulphides of all these metals are black. The lighter color of the Sulphides of the other metals may be entirely concealed by any of these black Sulphides. While it is useless to search for metals of the Lead and Copper class in a light-colored precipitate in the Second Group, the student is not to infer that the Arsenic and Tin bases must be absent from the black precipitates, but must determine their presence or absence by special investigation.

This Group is usually divided into two subdivisions, according to the solubility or insolubility of their Sulphides in NH_4HS .

First wash the precipitate, to remove any members of subsequent Groups, *If the precipitate is light colored*, it can contain only the members of the first subdivision (Sulphides soluble in NH_4HS .) and Cadmium. Boil a small quantity of the yellowish precipitate in a little solution of KHO: if a bright yellow precipitate remains undissolved, Cadmium is present; but if the precipitate dissolves, in part or in whole, a Sulphide of Antimony, Arsenic or Tin is present.

If the precipitate is black, mix a small quantity with NH_4HS . and heat gently: filter, and to the filtrate add a few drops of HCl.; if a yellow or orange precipitate forms (to be carefully distinguished from separated S.) the original precipitate contains both *the first and second subdivisions of Group II*, and the whole of the black precipitate must be treated with NH_4HS , filtered, and from the filtrate the members of the first subdivision be separated by the action of HCl.

The separation of the first and second subdivision may readily be effected as follows: treat the black precipitate with solution of $(NH_4)_2CO_3$. and filter off the ammoniacal solution, which will contain the Sulphides of Arsenic; wash the residual black precipitate and boil it in solution of KHO. which will dissolve all the Sulphides of Antimony and Tin. Filter and wash the precipitate still remaining, which will contain the second subdivision of Group II, while the filtrates secured by the Ammoniacal and Potassic solutions will contain the first subdivision, and these members may be recovered from the solutions by the action of HCl. which will precipitate them as Sulphides.

ANALYSIS OF FIRST DIVISION OF GROUP II.

Sulphides soluble in NH_4HS . but insoluble in dilute HCl .

[The Salts of Gold and Platinum belong in this Group and Subdivision, but they are seldom found in ordinary analysis, and are more readily identified by special methods than by systematic precipitation by Group Reagents. They will not be embraced in Group work, but the special tests for these bases will be given in their appropriate place.]

The members of First Division of Group II are:

As_2S_3 —bright yellow	{ Soluble in $(\text{NH}_4)_2\text{CO}_3$ Insoluble in HCl .	{ All soluble in a boiling solution of KHO .
SnS —Brown		
SnS_2 —Dirty Yellow	{ Soluble in Conc. HCl . Insoluble in $(\text{NH}_4)_2\text{CO}_3$.	
Sb_2S_3 } Orange		

ARSENIC. *To the Solution of Sulphide of Arsenic in $(\text{NH}_4)_2\text{CO}_3$. add HCl to the complete precipitation of As_2S_3 .* Separate and wash the yellow precipitate. Dry the precipitate and mix it with ten volumes of MnO_2 , place the mixture in a dry test tube and heat the salts to red heat. The As . will volatilize and condense upon the cold part of the tube in a white sublimate (often crystalline) of As_2O_3 . With a sharp file cut off the bottom of the tube (containing the brownish residue of MnO_2) and place the tube containing the white sublimate in a larger test tube containing distilled water, boil till the sublimate dissolves, and apply to this solution the special tests for As_2O_3 . The yellow Sulphide may easily be dissolved by adding a few drops of Conc. HCl . and placing in this a small fragment of KClO_3 , heat gently till solution is effected, and then boil till all oxides of Chlorine are expelled. For testing by Marsh's, Reinsch's or Bettendorf's test this form of solution is well adapted; for testing by Salts of Silver, Copper, &c., the solution of As_2O_3 is best.

Arsenic forms two classes of Salts—*Arsenious* and *Arsenic*—corresponding to As_2O_3 , trioxide, and As_2O_5 , pentoxide. The reactions will differ somewhat, according to the state of oxidation.

ARSENIOUS OXIDE. Solution of As_2O_3 , in presence of HCl , gives a **BRIGHT YELLOW PRECIPITATE OF As_2S_3 INSOLUBLE IN HCl . BUT READILY SOLUBLE IN $(\text{NH}_4)_2\text{CO}_3$.** This is one of the most delicate and characteristic tests for Arsenic, since one part of the Sulphide requires nearly 1,000,000 parts of water to dissolve it when HCl . is present. The only Sulphides that could be mistaken for As_2S_3 are CdS , SnS_2 , and Sb_2S_3 —but these are all insoluble in $(\text{NH}_4)_2\text{CO}_3$. in which As_2S_3 is soluble.

A solution of Arsenious trioxide in water gives a *green precipitate* of CuHAsO_3 (Scheele's Green) with Ammonio-Sulphate of Copper—soluble in HCl . and NH_4HO .

A watery solution of the trioxide will give a *yellow precipitate* (Ag_3AsO_3) with Ammonio-Nitrate of Silver, easily soluble in HNO_3 . and in NH_4HO . Ammonia water will dissolve many Arsenites, and the presence of Arsenical salts may easily be shown in this way. If wall papers containing the green Arsenite of Copper be moistened with a few drops of Ammonia water, and this

be squeezed out upon a white plate, and a crystal of AgNO_3 be dropped into the solution, a yellow precipitate around the crystal will show the presence of Arsenic.

Arsenic pentoxide. Solution of As_2O_5 is not immediately precipitated by H_2S in presence of HCl : but by the prolonged action of H_2S , the pentoxide is reduced to trioxide and precipitated as As_2S_3 . By boiling the Arsenic Acid or Arsenious with $\text{Na}_2\text{S}_2\text{O}_3$ the reduction to Arsenious condition is speedily effected, when addition of H_2S and HCl will cause the immediate precipitation of As_2S_3 ; this is sometimes obscured by separated Sulphur, in which case the As_2S_3 may be dissolved by NH_4HO , filtered from insoluble materials, and the Arsenious Sulphide precipitated from the filtrate by HCl .

Ammonio-Nitrate of Silver forms a BRICK-RED PRECIPITATE Ag_3AsO_4 —easily soluble in HNO_3 and in NH_4HO . If the Arsenic Acid contains an excess of HNO_3 , e.g. when the Sulphide has been oxidized and dissolved by HNO_3 add AgNO_3 to the clear solution and drop into this a crystal of Acetate of Sodium, when the characteristic brick-red Ag_3AsO_4 will form in the fluid surrounding the crystal.

Ammonio-Sulphate of Copper precipitates *light greenish-blue* Arsenate of Copper (Cu_3AsO_4) easily distinguished from Scheele's Green.

MgSO_4 in presence of NH_4HO and NH_4Cl precipitates Arsenic Acid in a white crystalline salt $\text{MgNH}_4\text{AsO}_4$. This salt closely resembles the corresponding Phosphate, but the Arsenate can readily be distinguished from the Phosphate by the method of reduction by boiling with the Hyposulphite of Sodium and precipitation of As_2S_3 by H_2S and HCl already pointed out—reactions not given by a Phosphate. If solution of Molybdate of Ammonia in excess be added to a solution of an Arsenate and the liquid warmed, a bright yellow precipitate of Arsenio-Molybdate of Ammonium will form, very similar to Phospho-Molybdate of Ammonium.

The Arsenites are much more common and important salts than the Arsenates. All the soluble or vaporous compounds of Arsenic are very poisonous.

REDUCTION TEST. If any dry compound of Arsenic be mixed with twenty times its volume of dry K_4Fcy , or a mixture of charcoal and KCy , and then heated in a closed glass tube a MIRROR OF METALLIC ARSENIC WILL FORM IN THE TUBE, AND A GARLIC ODOR MAY BE OBSERVED AT THE OPEN END OF THE TUBE. If this metallic mirror is gently heated while a current of air traverses the tube, the Arsenic will oxidize to As_2O_3 and deposit WHITE OCTOEDRAL CRYSTALS ON THE COOL PART OF THE TUBE [Use magnifying glass] The As_2O_3 may be dissolved in water, and the usual test applied.

REINSCH'S TEST. In mixtures containing organic matter, the soluble compounds of arsenic may most easily be separated by boiling the liquid with one-tenth its volume of HCl for a short time, to remove Nitrates, etc., then placing a slip of clean and bright Copper in the liquid and continuing the boiling for a few minutes. If any soluble compound of Arsenic is present, the metal will be precipitated on the surface of the Copper as a GRAY DEPOSIT OF ARSENIDE OF COPPER— Cu_3As_2 . If the Copper slip (or the gray scales, if much Arsenic was present) be withdrawn, washed, dried, placed in a dry test tube and heated red-hot, a part of the Arsenic will oxidize to As_2O_3 and form WHITE OCTOEDRAL CRYSTALS on the cool part of the tube.

MARSH'S TEST. Any soluble compound of Arsenic in presence of nascent Hydrogen will form Arsenetted Hydrogen— AsH_3 . In order to be assured of the purity of our materials and the absence of every trace of Arsenic from the chemicals employed it is desirable to perform a *blank experiment* by forming Hydrogen with the Zinc and Sulphuric acid, and testing the gas to see if it affords any indication of Arsenic; if Arsenical compounds are entirely absent, the liquid to be tested is then added to the Hydrogen generator, and the escaping gas tested for AsH_3 .

In this investigation the student will bear in mind that Hydrogen mixed in certain proportions with air becomes dangerously explosive in the presence of flame. Before heating the tube which conveys the escaping gas, or igniting the gas as it escapes he will wait till the Hydrogen has expelled the most of the air from the generator. He will also bear in mind that AsH_3 is poisonous and if breathed in large amount often causes fatal results.

A convenient generator for laboratory use may be made out of a wide-mouthed pint bottle with a tight-fitting cork having two perforations; through one a safety tube passes nearly to the bottom of the bottle, through which liquids may be poured into the bottle without removing the cork; through the other opening a tube of infusible glass passes through the cork, is bent above the cork at right angles so as to pass horizontally and the end is drawn down to a small jet. A half ounce of pure mossy zinc is placed in the bottle, four ounces of water and half ounce of C.P., H_2SO_4 are poured in, and the cork with its tubes inserted. If Hydrogen forms rapidly the air will be expelled from the bottle in one or two minutes, when the gas may safely be tested. Heat a part of the horizontal glass tube red-hot and see if any metallic deposit forms in the tube near the flame; at the same time light the Hydrogen escaping at the jet, and cut the flame with a cold surface of porcelain, and see if any brown spot forms on the porcelain. If no Arsenical deposits appear, pour into the bottle through the safety tube the liquid to be tested; heat the tube and cut the flame as before and watch results.

If a BROWN TO STEEL GRAY RING IS DEPOSITED WITHIN THE GLASS TUBE AND BEYOND THE FLAME, which is easily vaporized by heat, and in a current of air oxidized by heat to As_2O_3 : and if the flame cut by a cold porcelain surface forms BROWN, LUSTROUS SPOTS, READILY SOLUBLE IN SOLUTION OF NaClO , then Arsenic is present.

As Antimonetted Hydrogen, SbH_3 , may be formed under like conditions, and comports itself in many respects like AsH_3 , it is important to carefully distinguish between them. The following reactions will serve to distinguish these metals from each other:

<p><i>Arsenic deposit in tube.</i> Deposit BEYOND the flame. Easily vaporized by heat; does not melt.</p>	<p><i>Antimony deposit in tube.</i> Deposit BEFORE OR ON BOTH SIDES of the flame. Melts to small globules; vaporized at red heat.</p>
<p><i>Arsenic spots.</i> Lustrous brown gray to black. SOLUBLE IN NaClO. Dissolved by drops of HNO₃ when warmed. This solution with AsNO₃ and a little Ammonia gives a brick red precipitate.</p>	<p><i>Antimony spots.</i> Velvety brown to black. INSOLUBLE IN NaClO. Whitens but does not dissolve in HNO₃. Treated with AgNO₃ and a little Ammonia gives no color, but blackens when heated.</p>

The color of the spots, their solubility or insolubility in NaClO, the position of the deposit in heated glass tube, the difference in volatility, taken together serve to distinguish Arsenic from Antimony.

BETTENDORFF'S METHOD, MODIFIED. If any compound of Arsenic free from Sulphur, be placed in a concentrated solution of SnCl₂ to which half its volume of Conc. H₂SO₄ has been added (to set free fuming HCl.) and the whole heated to boiling, the Arsenic will be reduced to a metallic state FORMING A DEEP BROWN COLORATION, if the quantity is small, or a BROWNISH-BLACK PRECIPITATE if much Arsenic is present.

This reaction is very delicate, but requires the presence of *fuming HCl*. The compounds of Antimony do not give this reaction. This process will serve to distinguish between Arsenic and Antimony, or to detect Arsenic in the presence of a large amount of Antimony.

The following reactions, *taken together*, distinguish Arsenic from all other substances:

1. Formation of a black, shining sublimate by reduction.
2. Conversion of this sublimate into As₂O₃ by heating in a current of air.
3. Solution of this crystalline sublimate in water gives a yellow precipitate with H₂S. soluble in NH₄HO.
4. Formation of AsH₃ with deposit in heated glass tube, and lustrous brown spot on cold porcelain surface when its flame is cut, the spot soluble in NaClO.
5. Garlic odor when sublimate (1.) is heated in a small amount of air, or when the white sublimate (2.) is heated with reducing agents.
6. Production of brownish-black precipitate by boiling Conc. solution of SnCl₂ and H₂SO₄. (Bettendorff's Method.)

ANTIMONY AND TIN. From the Potassic solution of Sulphides, precipitate the Sulphides completely by HCl. wash the precipitate and dissolve in Conc. HCl. by aid of heat; if solution is milky from separated S., filter. If the precipitate from the Potassic solution by HCl. was orange color, Sb₂S₃ is present; if brown, SnS.; if a dingy yellow, SnS₂. These colors are not conclusive of the absence of Sulphides of a different color because a small amount of such Sulphides may be concealed by the color of associated Sulphides.

If the chlorides (of Antimony and Tin) formed by dissolving the Sulphides in Conc. HCl. be poured into a Hydrogen generator, the tin will be deposited on the Zinc as a spongy metallic mass, while a part of the Antimony will be con-

verted into gaseous SbH_3 , and if the flame of escaping gas be cut by a cold porcelain surface, a LUSTRELESS BLACK SPOT, INSOLUBLE IN NaClO is proof of the presence of Antimony. Remove the metals deposited on Zinc, wash them and heat with Conc. HCl . The Tin will dissolve and may be tested by HgCl_2 ; the Antimony will remain as black flakes or powder; wash and dissolve in Conc. HCl . with a small crystal of KClO_3 , and apply special tests.

SPECIAL TESTS FOR ANTIMONY. The salts of Antimony in presence of HCl are precipitated by H_2S . as an ORANGE-COLORED SULPHIDE, Sb_2S_3 , insoluble in dilute HCl , soluble in solution of KHO . If any acid salt of Antimony is boiled with $\text{Na}_2\text{S}_2\text{O}_3$, the Sulphide of Antimony is speedily deposited as a dark-red powder.

If any compound of Antimony be acidified with HCl . placed on a slip of Platinum foil and a fragment of Zinc dropped into the solution, the FOIL WILL BE STAINED BLACK BY DEPOSITION OF METALLIC ANTIMONY, insoluble in HCl . Under similar treatment Tin will be deposited *on the Zinc* in the form of a loosely adherent, dull gray powder, readily soluble in HCl .

If Chloride of Antimony be poured into a large volume of water, a white precipitate will form, $\text{SbCl}_3 + \text{H}_2\text{O} = \text{SbOCl} + 2\text{HCl}$. This oxychloride of Antimony is readily soluble in Tartaric Acid (distinction from BiOCl .)

When a small quantity of any compound of Antimony is supported on a thread of Asbestos and held in the upper reduction cone of a Bunsen burner, the flame becomes tinged bluish-white; if the flame is cut with a cold porcelain surface, a brownish-black spot of metallic Antimony is formed on the porcelain, insoluble in NaClO . If any compound of Antimony is heated on a carbonized match, brittle metallic globules will form on the match.

If any compound of Antimony be treated with Na_2CO_3 on charcoal before R.FI. white, brittle globules of Antimony will be obtained, and a white coating on the coal.

TIN. Tin forms two classes of salts—Stannous and Stannic—which have very different reactions with many reagents. Many chemicals will change the salts from one class to the other. For example the Stannous Sulphide is soluble in NH_4HS . but when precipitated from this solution by HCl . it is found in the form of Stannic Sulphide. When either Chloride of Tin is treated with metallic Zinc, the Tin is precipitated in the metallic form, and when the metal is dissolved in HCl . only SnCl_2 is formed. The degree of oxidation of the compounds of Tin must be determined *in the original solution*.

STANNOUS SALTS. In normal and not too acid solutions of Stannous Salts, H_2S . precipitates BROWN STANNOUS SULPHIDE, SnS . insoluble in NH_4HO . Soluble in Conc. HCl . in NH_4HS . and in KHO .

Stannous chloride PRECIPITATES HgCl_2 AS Hg_2Cl_2 . $\text{SnCl}_2 + 2\text{HgCl}_2 = \text{SnCl}_4 + \text{Hg}_2\text{Cl}_2$. In excess of SnCl_2 , the Hg_2Cl_2 is reduced to METALLIC MERCURY, FORMING A GRAY PRECIPITATE WHICH MAY BE GATHERED INTO A GLOBULE by boiling with HCl .

These reactions with H_2S . and HgCl_2 . are distinctive of Stannous Chloride.

Stannic Salts. Stannic Salts in presence of HCl . form a DINGY YELLOW PRECIPITATE with H_2S . of SnS_2 —insoluble in NH_4HO . but soluble in Conc. HCl . and in KHO .

Stannic Chloride does not reduce Mercuric Chloride.

If any compound of Tin be ground up with a mixture of equal parts of KCy and Na_2CO_3 . and exposed to R.FI. on charcoal, malleable globules of METALLIC TIN may be obtained.

ANALYSIS OF SECOND DIVISION OF GROUP II.

Sulphides insoluble in NH_4HS , and in KHO .

The members of Second Division of Group II are:

HgS —black: insoluble in HNO_3 .

CuS —black:

Bi_2S_3 —black:

CdS —yellow:

(PbS —black:)

} Soluble in HNO_3 .

Boil the Sulphides in dilute HNO_3 . If there is a black insoluble residue it is probably HgS . Filter from any insoluble residue. The solution may contain Cu_2NO_3 , Bi_2NO_3 , Cd_2NO_3 and Pb_2NO_3 . To a few drops of the solution add a drop of dilute H_2SO_4 ; if a white precipitate forms, add dilute H_2SO_4 to the whole solution and filter out PbSO_4 and apply to this the special tests for Lead given in Table VIII. To the filtrate or the solution from which H_2SO_4 does not form a precipitate, add NH_4HO to alkaline reaction; a white precipitate indicates Bismuth; filter; a blue solution indicates Copper, but it may also contain Cadmium, which by itself forms a colorless solution.

BISMUTH. Dissolve the white precipitate thrown down by NH_4HO in a small quantity of HNO_3 , and expel any excess of acid by boiling. Fill a test tube half full of water containing some NH_4Cl , and drop into this a few drops of the Nitrate of Bismuth; a WHITE PRECIPITATE (BiOCl) INSOLUBLE IN TARTARIC ACID shows the presence of Bismuth.

KHCrO_4 added to Salts of Bismuth precipitates a yellow basic chromate of Bismuth, soluble in HNO_3 (distinction from Lead).

H_2S produces a black precipitate of Bi_2S_3 , insoluble in dilute HCl and in NH_4HS but dissolved by HNO_3 .

Any compound of Bismuth heated on an Asbestos thread in upper reduction flame of Bunsen burner, forms a brown or black deposit upon a cold porcelain surface, cutting the flame: this coating of metallic Bismuth is only slowly dissolved by cold dilute HNO_3 . On a carbonized match, brittle globules of metallic Bismuth, which will break under the hammer.

If SnCl_2 is dissolved in excess of KHO (aided by heat), and to the clear solution a drop of any Salt of Bismuth is added and the mixture boiled, AN INTENSELY BLACK PRECIPITATE WILL FORM, Bi_2O_3 . Very delicate test.

All compounds of Bismuth are easily reduced to metallic state by heating in R.Fl. with Na_2CO_3 on charcoal, with a yellow coating on the coal.

COPPER. If the ammoniacal solution from precipitation of Bismuth is blue, it contains Copper. To confirm this, expel the ammonia by boiling, acidify with HCl , to a portion add K_4FCy : A REDDISH BROWN PRECIPITATE, INSOLUBLE IN HCl BUT SOLUBLE IN NH_4HO is proof of Copper.

In another portion of the solution place a bright piece of Metallic Iron: a DEPOSIT OF METALLIC COPPER on its surface is proof positive.

H_2S precipitates from Salts of Copper the brownish black CuS .

The Chloride of Copper colors flame first blue then green: all other Salts of Copper color the flame green.

Any compound of Copper on a Carbonized Match will yield red globules of Copper by Bunsen's flame method, the copper easily seen when the assay is

rubbed with a knife blade on a glass slip. The green flame is seen during the reduction.

Any compound of Copper is easily reduced to metallic state by treating with Na_2CO_3 on charcoal in R.Fl. The metal is melted into a globule only by a strong blast.

CADMIUM. If the solution (from separation of Bismuth) is colorless it may contain Cadmium. Add HCl. to acid reaction, and then H_2S . a **BRIGHT YELLOW PRECIPITATE, INSOLUBLE IN NH_4HO .**, but soluble in hot H_2SO_4 . is decisive of the presence of Cadmium. If the precipitate is brown or black (CuS .) add KCy to dissolve the Copper salt, when the yellow color of CdS . will appear if the metal is present.

Any compound of Cadmium, with Na_2CO_3 on charcoal before RFl. will give a **BROWNISH-RED COATING** to the coal, but no metallic globule.

Cadmium salts do not color the flame.

MERCURY. The black insoluble residue remaining after heating the sulphides of this subdivision with HNO_3 is probably HgS . Dissolve in hot Conc. HCl. with addition of a small crystal of KClO_3 . Boil to expel excess of acid, filter if necessary, and to a portion of the liquid add SnCl_2 . a **WHITE PRECIPITATE BECOMING BLACKISH-GRAY IN EXCESS OF SnCl_2** is proof of Mercury. This gray precipitate may be gathered into a globule by boiling with HCl.

Place a few drops of the solution on a clean slip of Copper, after a few minutes wash the Copper and rub the spot with a wet cloth; a **BRIGHT SILVERY SPOT, volatilizable by heat, is proof of Mercury.**

The action of H_2S . on a Mercuric salt is characteristic; a small amount may form a white precipitate, but increasing amounts of H_2S . **CHANGES THE COLOR TO YELLOW, ORANGE, RED, AND FINALLY TO BLACK.**

Solution of K I precipitates Mercuric salts, **AT FIRST SALMON COLOR, SPEEDILY BECOMING SCARLET.** The precipitate is soluble in excess of either the Mercuric salt or the Iodide.

In solution of a Mercuric salt NH_4HO forms a white precipitate NH_2HgCl . soluble in HCl.

If any dry compound of Mercury be ground in a mortar with its own volume of Potassium Iodide, Sodium Carbonate, and ten volumes of air-slacked lime, and the mixture be strongly heated in a dry test tube, a sublimate of HgI_2 —yellow to scarlet in color—will form on the cold part of the tube.

If any compound of Mercury be treated in the same way with omission of the Iodide, a gray tarnish of Mercury will form in the tube, visible as globules by magnifying glass, and may be united into larger globules by rubbing with a glass rod.

SPECIAL TESTS FOR GOLD AND PLATINUM.

Gold and Platinum are insoluble in HNO_3 and in HCl., but soluble in a mixture of these Acids=Aqua Regia. They are precipitated in the form of brownish-black sulphides by H_2S .—soluble in alkaline sulphides—soluble in Aqua Regia. Gold and Platinum are usually found in the metallic state (native) but Gold is often found in smaller quantity associated with metallic Sulphides. If these Sulphides are roasted to burn off the Sulphur the Gold may then be dissolved by heating with Aqua Regia, and the solution tested for the metal.

GOLD. Solution of a Salt of Gold is precipitated by solution of Fe_2SO in the **FORM OF FINELY DIVIDED METALLIC GOLD**. If the quantity of Gold is small the precipitate may remain suspended in the water for hours: appears brown by reflected light, and blackish blue by transmitted light.

If any solution of Gold be dropped on white paper and a drop of SnCl_2 dropped on the moistened spot, a rich purple color (Purple of Cassius) will appear.

If any solution of Gold moisten a piece of white paper (unglazed), this be dried and then burned so as to consume the carbon of the paper (or burn it white) a **PURPLE COLORATION** will appear whereon the Salt of Gold was applied. This is the most delicate test for Gold, and easiest of application.

The Chloride of Gold, even in dilute solutions, stains the skin a lasting purple color.

Any compound of Gold heated on a carbonized match in Bunsen's flame will form yellow malleable globules of metallic Gold. Heated with Na_2CO_3 on charcoal will give yellow globules of gold.

If a solution of Gold is boiled with Oxalic acid the gold is slowly but completely precipitated in metallic form (distinction from Platinum).

PLATINUM. Platinic Salts are precipitated as a **YELLOW CRYSTALLINE PRECIPITATE** (octohedral crystals) by KCl : ($\text{PtCl}_4\cdot 2\text{KCl}$) sparingly soluble in water; insoluble in alcohol. NH_4Cl forms a similar precipitate.

SnCl_2 imparts an *intensely dark brownish-red color to Platinic Salts from reduction to PtCl_2 .*

Any salt of Platinum heated on charcoal in R.Fl. yields a **GRAY INFUSIBLE, NON-MAGNETIC POWDER**, only soluble in Nitro-Hydrochloric acid.

Treated with a carbonized match in the Bunsen reduction flame the same result is secured.

TABLE X.

ANALYSIS OF GROUP III.

Substances whose normal and acid salts are not precipitated by H_2S in presence of HCl . but are completely precipitated by NH_4HS in presence of NH_4Cl and NH_4HO ,

The precipitate may contain :

CoS. } Black, insoluble in dilute HNO_3 .
NiS. }

FeS. Black.

MnS. Flesh-color.

ZnS. Dingy-white.

$Al_2(OH)_6$. Colorless and gelatinous.

$Cr_2(OH)_6$. Bluish green or peach-blossom.

Phosphates, Borates and Oxalates of Ba. Sr. Ca. Mg—white

All
Soluble in di-
lute HNO_3 .

The color of the precipitate may afford valuable hints in regard to its composition. If it is white it may contain Zinc and Alumina, (Phosphates, Borates and Oxalates of alkaline earths.): if pure flesh-color, Manganese: if light-colored, Iron, Nickel and Cobalt are all absent; but if it is black, all the members of the Group may be present, since the strong color of the black Sulphides will conceal the light-colored Sulphides and Hydroxides.

Separate the precipitate by filtering, wash the precipitate on the filter, and then pour over it dilute HNO_3 . A black and insoluble residue will be CoS. or NiS.

The filtrate may contain Iron, Manganese, Zinc, Aluminum and Chromium in the form of Nitrates. Add KHO in excess to this filtrate and boil. The precipitate will be hydroxides of Iron and Manganese. If a precipitate forms filter: wash the precipitate, dissolve in HCl. and apply tests for Iron and Manganese: the filtrate may contain Alumina, Chromium and Zinc. Add to it an excess of $Na_2S_2O_8$. and boil; a green precipitate will be $Cr_2(OH)_6$: separate this by filtering, wash it and dissolve in HCl. and apply tests for Chromium: add to the filtrate NH_4Cl in excess and boil; a white gelatinous precipitate shows presence of $Al_2(OH)_6$: filter, wash the precipitate, dissolve in HCl. and apply tests for Alumina: add to the filtrate H_2S in excess, which will throw down a whitish precipitate of ZnS. if Zinc is present.

Dissolve the (washed) precipitate thrown down by KHO. in HCl. add to this NH_4Cl in excess, and NH_4HO . to alkaline reaction: the REDDISH-BROWN PRECIPITATE is $Fe_2(OH)_6$: filter, and to the filtrate add H_2S . a FLESH-COLORED PRECIPITATE, MnS. shows the presence of Manganese. Dissolve the (washed) brown Ferric Hydroxide in HCl. and apply tests for Iron. Dissolve the flesh colored precipitate by H_2S in HCl. and apply tests for Manganese.

IRON. The Salts of Iron may exist in two states of oxidation—Ferrous and Ferric—exhibiting very different reactions with reagents according as they are in one or other state of oxidation. These salts are readily changed by reagents from one to the other state. By the treatment indicated in this Table the Salts will all appear in the Ferric condition. The original condition of the Salt can only be determined by tests applied to the original solution.

Ferric Salts are precipitated as brown Hydroxides by KHO. and by NH_4HO . With K_4FCy they form a **DEEP BLUE PRECIPITATE** $\text{Fe}_4(\text{FCy})_3$ or Prussian Blue, insoluble in HCl.

With NH_4CyS . they give a **BLOOD-RED COLOR**, but no precipitate.

With K_3Fdcy they give a greenish-brown color, but no precipitate.

With NH_4HS they form a black precipitate of FeS .

In the presence of HCl. Ferric Salts are not precipitated by H_2S . but a white precipitate of separated Sulphur is formed, with the reduction of the Ferric Salt to Ferrous.

Ferrous Salts tend to oxidize into the Ferric condition, and are with difficulty preserved in the Ferrous state.

With alkaline hydroxides they form Ferrous hydroxide, $\text{Fe}(\text{HO})_2$ —white, but rapidly becoming green, then rusty-red, by oxidation.

With K_4FCy they form a white precipitate, rapidly becoming blue, by oxidation.

With K_3Fdcy a **DEEP BLUE PRECIPITATE**, $\text{Fe}_3(\text{Fdcy})_3$, insoluble in HCl.

With NH_4CyS . Ferrous Salts do not form a precipitate or red color.

Any Salt of Iron treated with Na_2CO_3 on charcoal by R.Fl. gives infusible magnetic grains of metallic Iron.

The distinctive characteristics of Ferric and Ferrous Salts are that with K_3Fdcy the Ferrous salts form a deep blue precipitate—none with Ferric Salts: that NH_4CyS forms a red color with Ferric Salts—none with Ferrous.

MANGANESE. The most characteristic reaction for Manganese is the **FORMATION OF THE FLESH-COLORED** MnS . by NH_4HS . or by H_2S . is an ammoniacal solution. The least trace of Salts of Iron, Nickel or Cobalt will conceal the color by the formation of Black Sulphides.

KHO. precipitates $\text{Mn}(\text{HO})_2$ —white, becoming brown by oxidation.

If the Ammoniacal Solution of Manganese from which Ferric hydroxide has been precipitated, be boiled with solution of NaClO . the whole of the Manganese will separate as dark brown Sesquioxide.

Any compound of Manganese, free from Chlorides, boiled with PbO_2 and HNO_3 gives a **PURPLE COLORED SOLUTION** of Permanganic Acid.

Any compound of Manganese fused with KNO_3 and Na_2CO_3 on Platinum foil forms a **GREEN MASS** (h.) and **BLuish GREEN** (c.) of K_2MnO_3 . Very delicate reaction, and but little of Manganese should be used.

Any compound of Manganese fused with KClO_3 on Platinum foil gives a purple mass when cold.

Fused with a borax bead in O.Fl. Manganese gives a violet colored bead, best observed when only a little Manganese is used.

ALUMINUM. In the absence of Chromium compounds, the hydroxide of Aluminum is best precipitated by boiling the neutral or slightly acid solution with excess of $\text{Na}_2\text{S}_2\text{O}_3$. when all the Aluminum is thrown down as $\text{Al}_2(\text{HO})_6$ in form of a granular powder, rapidly subsiding, easily washed, and entirely free from Zinc. This is the easiest and best way of separating Aluminum from all associated metals except Chromium.

Aluminum hydroxide is readily soluble in KHO. Addition of NH_4Cl in excess and heating to boiling **WILL CAUSE PRECIPITATE** of $\text{Al}_2(\text{HO})_6$.

If any compound of Aluminum (except Silicate) is intensely heated before

the blow-pipe, moistened with Cobalt solution and again ignited, an **INFUSIBLE MASS OF SKY-BLUE COLOR** is produced. Decisive only with infusible bodies.

CHROMIUM. The salts of which Chromium is the base are precipitated in the form of $\text{Cr}_2(\text{HO})_6$ —dingy violet green—by NH_4HS ., and by KHO . soluble in excess of the latter **FORMING A GREEN SOLUTION**, precipitable by long boiling. The solution of Chromic-hydroxide in KHO . is speedily precipitated by boiling with $\text{Na}_2\text{S}_2\text{O}_3$.

Any compound of Chromium boiled in HNO_3 with a few grains of KClO_3 is soon oxidized to H_2CrO_4 , and the color of the solution changes to orange; if the acid be nearly neutralized with NH_4HO . and a few drops of solution of Pb_2NO_3 added, a **YELLOW PRECIPITATE** PbCrO_4 will be thrown down.

If any compound of Chromium is fused completely with KClO_3 and a little Na_2CO_3 on Platinum foil, the fused mass mixed with its volume of NaCl . this placed in a test tube and overflowed with Conc. H_2SO_4 . **RED VAPORS OF CrO_2Cl_2 WILL FORM IN THE TUBE, AND CONDENSE IN DARK-RED DROPS ON ITS SIDES.**

Chromic salts give an **EMERALD GREEN BEAD IN BOTH FLAMES** with borax bead.

The acids of Chromium, in the presence of HCl ., are reduced to basic condition by H_2S . In the analysis of Chromates, the Chromium is usually reduced and detected as a basic substance. The salts in which Chromium is the base are usually violet or green in color, but the salts in which it acts as an acid are usually yellow or red. The great variety of colors gives the name Chromium—the color metal.

ZINC. The salts of Zinc are precipitated as hydroxide by NH_4HO . readily soluble in excess. From this solution H_2S . **PRECIPITATES THE DINGY WHITE ZnS .**

If any compound of Zinc is treated with Na_2CO_3 on charcoal in R.Fl. the charcoal will be **COATED WITH INCRUSTATION, YELLOW (h.) WHITE (c.)**, without the formation of a metallic globule.

If ZnO is moistened with Cobalt solution and heated in O.Fl. **A GREEN COLOR IS PRODUCED.**

Examine some of the black sulphides insoluble in HNO_3 with a borax bead in blowpipe flame. **A BLUE BEAD IN BOTH FLAMES** shows the presence of Cobalt: **A REDDISH BEAD IN O.Fl. BECOMING GRAY AND CLOUDED** in R.Fl. shows presence of Nickel. The strong coloring property of Cobalt with borax may conceal the presence of Nickel.

Puncture the bottom of the filter with a glass rod and wash the black sulphides into a test tube. Add conc. HCl . and a small amount of KClO_3 and dissolve with aid of heat; filter if necessary.

If both Cobalt and Nickel are present their separation may be effected in two ways.

SEPARATION OF NICKEL AND COBALT.

1. Add NH_4Cl in excess, then K_3Fdcy in quantity sufficient for complete precipitation, and then NH_4HO in excess, when the whole is well shaken: filter, when the Cobalt remains upon the filter as Ferricyanide of cobalt (cop-

per-red), while Nickel is found in the filtrate, from which it can be precipitated by NH_4HS .

2. If the mixed Chlorides of Nickel and Cobalt be treated with KCy and boiled for a few minutes to convert the Cobalt into Cobalticyanide, then KHO added in excess, and to this a solution of NaClO be added and the mixture boiled, all the Nickel is precipitated as black Ni_2O_3 . If the quantity of Nickel is small, an inky coloration will show its presence. So delicate is this reaction that all the commercial salts of Cobalt will show this reaction for Nickel.

NICKEL. Salts of Nickel have usually a fine green color. They are precipitated as NiS —black—by NH_4HS . the precipitate very sparingly soluble in NH_4HS *imparting a brown color to the filtrate*. They are precipitated as bluish green hydroxide $\text{Ni}(\text{HO})_2$ by NH_4HO . very soluble in excess and forming a violet blue solution.

$(\text{NH}_4)_2\text{C}_2\text{O}_4$ precipitates very slowly, but almost completely after 24 hours, the green NiC_2O_4 .

The salts of Nickel are completely precipitated by boiling with NaClO in presence of KHO . **AS BLACK PEROXIDE OF NICKEL.** Very delicate and decisive test.

Any compound of Nickel treated with Na_2CO_3 on charcoal in R.Fl. gives infusible metallic Magnetic grains of Nickel.

COBALT. Alkaline Sulphides precipitate the black CoS .

Solution of KHO precipitates $\text{Co}(\text{HO})_2$ (blue but becoming green by oxidation) insoluble in excess.

NH_4HO forms same precipitate, soluble in excess, forming reddish brown solution

Salts of Cobalt are precipitated by K_3Fdcy as **A DARK COPPER-RED PRECIPITATE** $\text{Co}_3(\text{Fdcy})_2$.

$(\text{NH}_4)_2\text{C}_2\text{O}_4$ precipitates Salts of Cobalt in the form of reddish white Oxalate, CoC_2O_4 , soluble in HCl . and in NH_4HO .

Bead of borax with any compound of Cobalt **GIVES A BLUE BEAD IN BOTH BLOWPIPE FLAMES.**

If a salt of Cobalt be reduced on a carbonized match in Bunsen's reducing flame, shining white magnetic grains are obtained, soluble in HCl forming a rose-red solution.

SPECIAL OPERATIONS REQUIRED WHEN PHOSPHORIC, ARSENIC, AND OXALIC ACIDS ARE PRESENT.

When Phosphates, Arsenates, etc., of Aluminum, Iron, Barium, Strontium, Calcium or Magnesium are present they will be precipitated by NH_4HS . because these salts are insoluble in an alkaline fluid.

Dissolve the washed precipitate in HNO_3 and boil: add $\text{Hg}_2\text{2NO}_3$; a white precipitate indicates an Oxalate. The Oxalates may be decomposed by igniting on Platinum foil, when the bases will be left in the form of Carbonates.

Add two drops of the Nitric solution to 20 drops of Molybdate of Ammonia and heat gently: an intense yellow color or yellow precipitate shows presence of Phosphoric or Arsenic Acid. In such case add Ferric Chloride and Sodium Acetate to the solution, boil and filter while hot. The precipitate will contain the Phosphoric, etc., Acid in insoluble combination with the Iron, while the Alkaline earths will appear in the filtrate in the form of Acetates.

TABLE XI.

ANALYSIS OF GROUP IV.

Substances not precipitated by NH_4HS , but completely precipitated by $(\text{NH}_4)_2\text{CO}_3$ in the presence of NH_4Cl .

The precipitate may contain

BaCO_3 SrCO_3 CaCO_3	}	White, soluble with effervescence in Acetic Acid.
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Wash the precipitate and dissolve in Acetic Acid.

To a small portion of this solution add a few drops of KHCrO_4 : if a **YELLOW PRECIPITATE FORMS** it shows the presence of Barium. In such case filter off BaCrO_4 and divide the filtrate into two parts: to one add its own volume of solution of CaSO_4 and shake the mixture thoroughly and repeatedly to promote precipitation.

If no precipitate forms set the tube aside for ten minutes; a **WHITE PRECIPITATE** shows presence of Strontium. If no precipitate forms at the end of ten minutes, **ABSENCE OF STRONTIUM**.

If Strontium is absent, add to the other portion of the solution $(\text{NH}_4)_2\text{C}_2\text{O}_4$: a **WHITE PRECIPITATE** insoluble in Acetic acid but soluble in HCl shows presence of Calcium. But if Strontium is present, first add K_2SO_4 to the other part of the filtrate, boil for a few minutes, filter, and add $(\text{NH}_4)_2\text{C}_2\text{O}_4$ to the clear filtrate: if a precipitate now forms, Calcium is present: if no precipitate Calcium is absent.

BARIUM. From Salts of Barium H_2SO_4 **THROWS DOWN A WHITE, HEAVY PRECIPITATE INSOLUBLE IN WATER AND IN HCl ; BaSO_4 .**

From $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ solution of KHCrO_4 precipitates BaCrO_4 , **YELLOW SALT INSOLUBLE IN $\text{HC}_2\text{H}_3\text{O}_2$.**

H_2SiF_6 precipitates BaSiF_6 as a **WHITE CRYSTALLINE PRECIPITATE** (distinction from Strontium and Calcium).

Solution of CaSO_4 precipitates the salts of Barium *instantly*—of Strontium *only after an interval*—and of Calcium *not at all*.

BaCl_2 **COLORS THE GAS FLAME YELLOW GREEN.**

STRONTIUM. Concentrated solution of a salt of Strontium is precipitated by H_2SO_4 , SrSO_4 —white—soluble in 5000 parts of water. Solution of CaSO_4 **GIVES A TARDY PRECIPITATE** with salts of Strontium.

$(\text{NH}_4)_2\text{C}_2\text{O}_4$ forms a white precipitate insoluble in Acetic Acid.

The Nitrate and Chloride of Strontium **COLOR THE GAS FLAME DEEP RED: VIEWED THROUGH BLUE GLASS THE COLOR IS ROSE-RED.**

CALCIUM. In concentrated solutions of salts of Calcium, H_2SO_4 and alkaline Sulphates precipitate CaSO_4 soluble in 400 parts of water. Solution of CaSO_4 of course will give no precipitate with salts of Calcium.

In absence of salts of Barium and Strontium, the most delicate test for salts of Calcium is $(\text{NH}_4)_2\text{C}_2\text{O}_4$, which throws down a **WHITE PRECIPITATE, INSOLUBLE IN ACETIC BUT SOLUBLE IN HYDROCHLORIC ACID.** This Oxalate of Calcium requires 200,000 parts of water to dissolve it.

Nitrate and Chloride of Calcium **COLOR THE GAS FLAME ORANGE-RED**—often mistaken for the crimson color of Strontium, but when viewed through blue glass the color is faint green-gray.

TABLE XII.

ANALYSIS OF GROUP V.

Substances not precipitated by Group Reagents.

This group includes

Potassium.	} Alkali Metals.
Sodium.	
Ammonium.	
Magnesium.	

Divide the filtrate from which $(\text{NH}_4)_2\text{CO}_3$ will not produce a precipitate, into two parts: to one add Na_2HPO_4 and shake thoroughly: If no precipitate forms, rub the inside of the test tube with a glass rod and set aside the test tube for a few hours. **A WHITE CRYSTALLINE PRECIPITATE SHOWS THE PRESENCE OF MAGNESIUM.** In very dilute solutions the precipitate forms only after the lapse of several hours.

Evaporate the other part of the filtrate to dryness and heat red hot on Platinum foil to expel all salts of Ammonium. If a solid residue, dissolve in a few drops of water, moisten a clean Platinum wire in this solution and place it in the gas flame: **A PURPLE COLOR OF THE FLAME INDICATES POTASSIUM: A BRILLIANT YELLOW, SODIUM.**

MAGNESIUM. The salts of Magnesium do not color the flame.

The **WHITE CRYSTALLINE PRECIPITATE** formed by Na_2HPO_4 in presence of NH_4Cl and NH_4HO is most characteristic of Magnesium.

The Sulphate of Magnesium is very soluble in water, which distinguishes this metal from those of the Alkaline Earths.

If any compound of magnesium be heated to redness on charcoal then moistened with solution of Cobalt, and again heated, at first gently, and then intensely in O.F. **A PINKISH MASS IS OBTAINED.** Alkalies and Alkaline Earths prevent this reaction.

KHO precipitates Magnesium hydroxide, $\text{Mg}(\text{HO})_2$ from salts of Magnesium. NH_4Cl prevents this reaction.

Alkaline Carbonates precipitate basic Carbonates in absence of NH_4Cl .

POTASSIUM. The most characteristic test of Potassium is the **VIOLET COLORED FLAME**—best seen with the Chloride. If Sodium is present the intense color of this yellow flame obscures the feebler color of the potassium flame, but by the use of the blue Cobalt glass the yellow rays are intercepted, and then the characteristic color of the Potassium flame can be observed.

Tartaric Acid added in excess to a concentrated Potassium salt will form a **WHITE CRYSTALLINE PRECIPITATE.**— $\text{KHC}_4\text{H}_4\text{O}_6$. Ammonium forms a similar salt. PtCl_4 added to KCl forms a **YELLOW CRYSTALLINE PRECIPITATE.** K_2PtCl_6 . The crystals under the microscope are seen to be octohedrous, or 8 faced crystals.

Ammonia forms a similar precipitate with Platinic Chloride.

The tests by precipitation for Potassium, therefore, are decisive only after all the compounds of Ammonium have been expelled by heating the residue red hot.

SODIUM. There is no satisfactory precipitant for salts of Sodium. The **BRILLIANT YELLOW FLAME REACTION** is most satisfactory, and is relied on for the detection of the compounds of Sodium.

AMMONIUM. The Salts of Ammonium having been freely used as reagents in the separation of the Groups, and the salts thus employed all appearing in the successive filtrates, their presence in the final filtrate is no proof that they existed in the original solution. For these reasons *the original solution must be tested for this substance.*

Any salt of Ammonium boiled with KHO WILL GIVE OFF GASEOUS AMMONIA, NH_3 , *readily recognized by its odor, by its alkaline action on red litmus paper, and by forming white fumes when a rod moistened with Conc. HCl. is held near the escaping gas.*

If any salt of Ammonium (in the absence of Sulphides and Cyanides) be added to Nessler's Test, a **BROWN PRECIPITATE**, $\text{NH}_2\text{Hg}_2\text{Cl}$, will form, or if the quantity is very small, a brown coloration in the liquid. Very sensitive test. Nessler's Test is prepared as follows:

To a solution of HgCl_2 , add solution of KI. till the scarlet precipitate— HgI_2 —at first formed, is *nearly* all redissolved; then add KHO: let the mixture stand till all sediment subsides, then pour off the clear liquid for Nessler's Test.

As the preparation of this test requires care and time, the student will not prepare it for himself, but will find it ready for use among the select reagents. Only a few drops are necessary to test for Ammonium, and excess of the reagent will not produce better results.

If NH_4HO . or $(\text{NH}_4)_2\text{CO}_3$ is added to solution of HgCl_2 "**WHITE PRECIPITATE**" of NH_2HgCl will form (Bohlig's Test). This test is extremely delicate, and will often serve to detect the presence of Ammonia in rain water and other natural waters.

If Ammonium is in too small amount to be detected by these tests, it may yet be found by distilling the water with KHO. and testing the distillate.

ANALYSIS OF ACIDS.

After the bases have been identified, the next step in analysis is to identify the acids. In this investigation great assistance may be derived in regard to the probable presence or absence of many of the acids by consulting Table XIII of Solubilities. For example, if we have found Barium in a soluble compound, or a compound soluble in HCl, there is no need of seeking for H_2SO_4 , because $BaSO_4$ is insoluble in water and acids. If we have found Silver, there is no use of seeking for HCl, HBr, HI, H_2S , H_4Fcy , or H_3Fdcy , because the Silver salts with these Acids are all insoluble. On the other hand, the Nitrate and Acetate of Silver are soluble, and Silver may therefore be present in the form of Nitrate or Acetate.

Again, if a lime salt is but sparingly soluble in water, and its solubility sensibly increased by HCl, the Table shows this is characteristic of the Sulphate.

The Acid combinations of Arsenic, Antimony and Chromium will have been detected in the examination for bases; the acid combinations of these metals will not, on this account, be fully treated in speaking of the Analysis of Acids.



PRELIMINARY EXAMINATION OF THE SOLID SUBSTANCE FOR ACIDS.

Successive Steps in Preliminary Examination.

1st. Heat some of the dry substance red-hot on Platinum foil: Chars and form combustible vapors. Organic substance. The organic acids present may be Acetic, Tartaric, Citric, etc., Hydroferrocyanic, Hydroferricyanic, (and Cyanides of heavy metals).

2nd. Place some of the substance on charcoal and heat in O.F.I:

Deflagration ensues; presence of Chlorates, Chromates, Manganates, Nitrates, or Permanganates. Should this reaction (deflagration) take place, the treatment under 4th step must be omitted to avoid explosions likely to occur with chlorates.

3d. Place some of the substance in a test tube, overflow it with twice its volume of dilute H_2SO_4 , and if no change ensue heat to boiling.

Effervescence liberating:

Carbonic.— CO_2 —Odorless—turns lime water turbid, forming $CaCO_3$.

Sulphurous.— SO_2 —Odor, burning sulphur, bleaches litmus paper.

Hyposulphurous. $\left. \begin{array}{l} SO_2 \\ \text{and} \\ H_2S \end{array} \right\}$ Odor, burning sulphur and rotten eggs, bleaches litmus paper; Sulphur separates in solution.

Hydrosulphuric.— H_2S .—Odor, rotten eggs. Blackens lead paper.

No change taking place in the cold, the tube is heated to boiling and any volatile acid expelled. These acids may be:

Hydrocyanic.—Detected by characteristic odor of a bruised peach leaf.

Acetic.—Detected by odor of vinegar.

Hydrochloric. $\left\{ \begin{array}{l} \text{Detected by white fumes, formed by holding glass rod moistened with } NH_4HO \text{ at the mouth of the tube. (The first} \\ \text{two fumes strongly, the last two slightly.)} \end{array} \right.$
Nitric.
Hydriodic.
Hydrobromic.

4th. The finely powdered substance is mixed with half its volume of MnO_2 , placed in a test tube, overflowed with Conc. H_2SO_4 and heated to a temperature less than the boiling point of the Sulphuric Acid.

Hydrobromic: brown vapor of Bromine.

Hydriodic: violet vapor of Iodine.

Hydrochloric: yellow-green gas. Chlorine. This gas poured into another tube containing water, agitated—a drop of $AgNO_3$ produces curdy white precipitate, $AgCl$.

Hypochlorous: yellowish gas, Cl_2O : bleaches indigo solution.

Hydrofluoric: white fumes; etches glass; does not precipitate $AgNO_3$.

Nitric. $\left\{ \begin{array}{l} \text{Orange-red fumes evolved.} \end{array} \right.$
Nitrous.

Oxalic: colorless gas escapes (CO_2) with effervescence. Test with lime water.

If, in this preliminary examination, evidence is obtained of the presence of certain acids, the special tests for these acids (given in the succeeding pages) may be at once applied, without resorting to the use of Group-Reagents for the classification of acids. But in the absence of any such special indications, the Group-Reagents must be employed for the separation and identification of the acids.

SEPARATION AND CLASSIFICATION OF ACIDS.

The substance for analysis being in solution (thus preventing the use of the preliminary examination for acids), or the preliminary examination failing to show any indications of the acids present, the analysis for acids is commenced by a separation into groups, in a manner similar to the separation of bases.

In the analysis of the bases, many reagents have been applied containing substances whose presence in the final filtrate from the fifth group of bases would be no proof that they existed in the original substance or solution. In the analysis of acids, therefore, *the original substance must be employed*. It is also apparent that where HCl, HNO₃, etc., have been used to dissolve the substance for analysis, their presence must be borne in mind in testing for the acids.

The acids can not be separated into groups with the precision with which we separate bases; yet the selection and identification of acids are greatly facilitated by proper grouping. The presence of bases of the I, II, III and IV Groups may interfere with the reactions of the Acid Group Reagents. It is often desirable to separate these bases before making analysis of the acids, especially if several acids are present. These bases may be separated by boiling the solution with Na₂CO₃ in excess, filtering off the separated bases, and adding to the filtrate just enough HNO₃ to make it neutral, and boiling the solution to expel CO₂, the acids will then be present in the form of Salts of Sodium.

It must be borne in mind that by this method of treatment CO₂ will be removed and HNO₃ has been added. The original substance, therefore, must be tested for the presence of these acids and not the solutions prepared as indicated in the preceding paragraph.

CLASSIFICATION OF ACIDS.

In the analysis of Acids we employ *Group-Reagents* (as with bases) to classify them, and *Special Reagents* to identify the individual acids. The Group-Reagents are Ba₂NO₃, Ca₂NO₃, AgNO₃, and Fe₂Cl₆.

GROUP A.

Add to the neutral Solution Ba₂NO₃ to complete precipitation: if no precipitate forms, all the following acids are absent: if a precipitate forms, any of the following acids may be present:

Precipitate.

a.	{	Chromate of Barium—yellow	} Soluble in HNO ₃ .
		Carbonate " " —white.	
		Phosphate " " "	
		Silicate " " "	
		Sulphite " " "	
		Oxalate " " "	

b.	{	Sulphate of Barium—white	} Insoluble in HNO ₃ .
		Fluosilicate " " "	

In the absence of salts of Ammonium, the precipitate may be:

Arsenite	} of Barium, white.
Borate	
Tartrate	

If a precipitate forms, add HNO_3 . If it does not all dissolve, filter. The insoluble precipitate shows the presence of Sulphuric or Fluosilicic acid. Add to the filtrate NH_4HO to alkalinity, if a precipitate forms, any or all the acids in sub-division a. may be present. Should the precipitate when treated with HNO_3 , effervesce, the presence of Carbonic acid would be indicated.

GROUP B.

Add to the original (neutral) solution Ca_2NO_3 to complete precipitation. White precipitate, shows presence of

- | | | |
|----|--|---------------------------------------|
| a. | $\left\{ \begin{array}{l} \text{Sulphate} \\ \text{Sulphite} \\ \text{Carbonate} \\ \text{Phosphate} \\ \text{Oxalate} \\ \text{Fluoride} \\ \text{Silicate} \end{array} \right\}$ | Insoluble in NH_4Cl . |
| b. | $\left\{ \begin{array}{l} \text{Borate} \\ \text{Tartrate} \end{array} \right\}$ | Soluble in NH_4Cl . |

If precipitate forms add NH_4Cl ; if it does not all dissolve, filter, and add to insoluble residue (a.) Acetic acid:

Dissolved.

Carbonate (effervescence).
Phosphate.
Sulphite.
Silicate.

Undissolved.

$\left. \begin{array}{l} \text{Sulphate} \\ \text{Oxalate} \end{array} \right\}$ White and pulverulent.
 Fluoride, gelatinous.

GROUP C.

Add to the original solution AgNO_3 .

If no precipitate form, all the following acids are absent: if precipitate forms, the color may give a useful hint.

Precipitate WHITE:

Bromide.
Chloride.
Cyanide.
Carbonate.
Sulphocyanide.
Oxalate.
Iodide (yellowish white).
Ferrocyanide (yellowish white).

Precipitate YELLOW:

Phosphate.
Arsenite.

Precipitate RED:

Chromate.
Arsenate.
Ferricyanide—brown.

Precipitate BLACK:

Sulphide.
Sulphite (dirty brown).

If the precipitate is white or yellowish white, boil it with dilute HNO_3 . A residue will show the presence of a Chloride, Bromide, Iodide, Cyanide or Sulphocyanide. Allow the residue to subside, pour off the HNO_3 and add NH_4HO , which will dissolve all except the Iodide.

If the precipitate is yellowish white, and changed to brown by boiling in HNO_3 , the brown salt soluble in NH_4HO , a Ferrocyanide is present, (changed to Ferricyanide by boiling with HNO_3).

GROUP D.

Add to the original solution Fe_2Cl_7 .

Precipitate deep blue Ferrocyanide.

Precipitate yellowish white, insoluble in Acetic Acid Phosphate.

Brown coloration, no precipitate, Ferricyanide.

Blood-red coloration (not changed by HCl), Sulphocyanide.

Blood red coloration, disappearing rapidly on addition of HCl and boiling—Sulphite.

Brownish-red color—quickly destroyed by HCl , Acetate.

It will be observed that many acids appear in the precipitates of two or more groups and it would at first seem to be impossible to separate out and recognize the various acids under these circumstances. But if the analyst will carefully compare the precipitates obtained by the four operations under Groups A, B, C and D he will, at the end of such comparative study, have a reasonable clue by which he may proceed to apply Special Reagents for the various precipitable Acids.

**SPECIAL REACTIONS WITH THE ACIDS PRECIPITATED
By Ba₂NO₃ and by Ca₂NO₃.**

ARSENIOUS AND ARSENIC: These acids are separated and identified in analysis of the bases. Arsenious acid is distinguished from Arsenic acid by a mixture of NH₄HO and AgNO₃ (Ammonia Nitrate of Silver) which forms with Arsenious acid a yellow precipitate, while with Arsenic acid it forms a brick red.

BORIC: If conc. HCl is added to a Borate and Turmeric paper be moistened with this solution, THE PAPER ON DRYING IS STAINED BROWNISH-RED. If conc. H₂SO₄ is added to a Borate, alcohol poured on this in a watch glass and the mixture ignited, the flame is tinged yellowish green. Acid Borates form a white precipitate of Ag₃BO₃ with AgNO₃. Neutral Borates form brown oxide of Silver.

CHROMIC: Chromic acid is often reduced and separated as a base in analysis. The color of chromates is yellow or red. (The acid salts being red.) From solution of Ba₂NO₃, Chromates precipitate YELLOW. BaCrO₄, from Pb₂NO₃, YELLOW PbCrO₃ (this reaction is assisted by presence of HNO₃); from Hg₂NO₃, DARK RED Hg₂CrO₄. If any Chromate is boiled with conc. HCl and Alcohol, Cr₂Cl₆ will be formed, coloring the solution intensely green. Any Chromate heated with conc. H₂SO₄ and NaCl in a test tube evolves red vapor of Chromyl Chloride CrO₂Cl₂.

CARBONIC: Carbonates are decomposed by dilute HCl. the decomposition attended by a BRISK EFFERVESCENCE of CO₂. When this gas is poured into a clean test tube, a little Lime water added and shaken up, a white precipitate forms CaCO₃—. Solutions of Carbonates precipitate Ca₂NO₃, forming CaCO₃, readily soluble in dilute HCl with effervescence.

HYDROFLUORIC: The most characteristic reaction of this acid is its power to etch glass. If a finely powdered Fluoride is made into a paste with conc. H₂SO₄ in a lead crucible, the crucible covered with a piece of glass coated with beeswax, in which lines have been traced with a sharp point of wood, laying bare portions of the glass surface, and the crucible gently warmed for an hour, upon removing the wax by scraping and washing with turpentine, the exposed lines will be found ETCHED INTO THE GLASS. If the quantity of Fluoride was small the etching may be invisible, but will appear by breathing on the glass. If a powdered Fluoride mixed with powdered Silica be placed in a dry test tube, overflowed with conc. H₂SO₄ and gently heated, dense white fumes of Hydrofluosilicic acid will escape into the air.

PHOSPHORIC: If to a solution of a Phosphate a few drops of HNO₃ are added and then about 20 drops of Molybdate of Ammonium and the mixture warmed up, an INTENSE YELLOW PRECIPITATE WILL BE FORMED. The solution of the phosphate must not be too concentrated, or the precipitation will not occur. (Arsenic acid produces a similar precipitate). A Phosphate is precipitated by MgSO₄ in presence of NH₄Cl+NH₄HO,

forming a white (chrystalline when viewed with a lens) precipitate $\text{NCgNH}_4\text{PO}_4$. In very dilute solutions the precipitate forms only after a time; promoted by briskly agitating the solution and rubbing the inside of the test tube with a glass rod. Ammonio-Nitrate of Silver forms a yellow precipitate, Ag_3PO_4 (distinction from Arsenate which forms brick-red.) Fe_2Cl_6 added to a solution of a neutral Phosphate precipitates a **YELLOWISH-WHITE FLOCCULENT** $\text{Fe}_2\text{2PO}_4$, **INSOLUBLE IN ACETIC ACID**.

OXALIC: If Ca2NO_3 is added to Oxalic Acid or an Oxalate (in absence of free acids) a white, pulverulent precipitate of Oxalate of Calcium will form, insoluble in Acetic (distinction from Carbonic), soluble in HCl . If Oxalic acid or an Oxalate is mixed with powdered MnO_2 (free from Carbonate) water added, and a little conc. H_2SO_4 , a **LIVELY EFFERESCENCE** occurs, caused by escape of CO_2 , the Oxalate being decomposed.

SILICIC: Only the alkaline Silicates are soluble. If to an (not too dilute) solution of an alkaline Silicate NH_4Cl is added the Silica will be precipitated because an alkaline chloride is formed, and Silica does not enter into combination with NH_4HO set free by the reaction. If HCl is added to a concentrated solution of an alkaline Silicate, the solution **SETS INTO A JELLY-LIKE MASS** from formation of Hydrate of Silica. But if HCl in excess is added at once to a not too concentrated solution of a Silicate the Silicic Acid remains in solution; if this solution is evaporated to dryness, the white powder insoluble in HCl is Silica. The Silica is soluble in a boiling solution of KHO . In the solid state Silica is best recognized by bead with Microcosmic salt, forming skeleton of Silica.

SULPHURIC: The reaction with Ba2NO_3 , giving a white precipitate insoluble in HCl is very characteristic of Sulphuric acid and Sulphates. A similar precipitate is formed by Selenic and by Fluosilicic Acid; but these acids are so rare that the above reaction with Barium Nitrate is usually accepted as proof of the presence of Sulphuric Acid.

SULPHUROUS: When heated this acid exhales the **STIFLING ODOR OF BURNING SULPHUR**. A Sulphite treated with HCl and heated exhales the same odor. Fe_2Cl_6 added to Sulphurous Acid or a Sulphite forms a blood-red color, which disappears on adding HCl and boiling. AgNO_3 precipitates a sulphite, dirty-white, becoming black by boiling. Moist blue litmus paper held in SO_2 escaping from the decomposition of a Sulphite by an acid is first reddened and then bleached.

ACIDS DETECTED BY NITRATE OF SILVER.

HYDROBROMIC: Watery solutions of Hydrobromic acid and soluble Bromides produce a yellowish-white precipitate with AgNO_3 , insoluble in HNO_3 , somewhat difficultly soluble in NH_4HO . If conc. H_2SO_4 and MnO_2 be added to any Bromide, and the mixture heated, **BROWNISH-RED VAPORS OF BROMINE** are evolved. The color is best observed by looking lengthwise through the test tube. If solution of Starch is brought in contact with Bromine yellow Bromide of Starch is formed.

HYDROCYANIC: HCy gas has the odor of bruised peach leaves. If a finely powdered Cyanide be placed in a watch glass, moistened with conc. HCl , and another watch glass having a drop of NH_4HS on its concave surface be inverted over this, and the whole slightly warmed, HCy will be set free—uniting with the NH_4HS to form NH_4CyS . If the second watch glass be carefully dried, the residue moistened with HCl and a drop of Fe_2Cl_6 added, a deep blood red coloration will be formed. To detect Hydrocyanic Acid and Cyanides in solution the solution is first rendered strongly alkaline with KHO , a small quantity of Ferroso-ferric Sulphate (mixture of Ferrous and Ferric Sulphate) added and the whole warmed for a short time (to assist the formation of K_4Fcy) then an excess of HCl added, Prussian blue is formed if a Cyanide is present, or if in very small quantity the liquid assumes a green color and deposits Prussian blue after a time. To detect HCy in Cyanides which do not give off HCy when treated with an acid, they must first be fused with Na_2CO_3 on Platinum foil, the mass boiled with water and the solution tested with Ferroso-Ferric Sulphate as given above.

HYDROFERROCYANIC: Best detected by Fe_2Cl_6 . The Ferrocyanide of Silver is yellowish white, soluble with difficulty in NH_4HO : insoluble in boiling HNO_3 but converted by it into Ferricyanide of Silver (brown).

HYDROFERRICYANIC: Best detected by Ferrous salt. The Ferricyanide of Silver is of a brownish red color, insoluble and unchanged by HNO_3 even when boiled with it, readily soluble in NH_4HO .

The reactions of Iron salts with both these acids are so very characteristic and easily secured that Silver is seldom used for their identification.

HYDROCHLORIC: With HCl or soluble Chlorides AgNO_3 produces a **CURDY WHITE PRECIPITATE**, AgCl . By prolonged exposure to sunlight it becomes violet and finely black. It is insoluble in HNO_3 , readily soluble in NH_4HO . Mercurous Nitrate forms a white precipitate, Hg_2Cl_2 , with HCl or soluble Chlorides, insoluble in HNO_2 or NH_4HO . but blackened by the latter. Any Chloride heated with conc. H_2SO_4 and MnO_2 evolves **CHLORINE GAS**—recognized by odor, color and bleaching properties. If the gas is poured into a tube containing a little water, the tube agitated and a drop of AgNO_3 added, a curdy precipitate of AgCl will be formed.

HYDRIODIC: With HI or soluble Iodides, AgNO_3 precipitates AgI **YELLOWISH WHITE INSOLUBLE IN BOTH HNO_3 AND NH_4HO** . A mixture of CuSO_4 and FeSO_4 precipitates from solutions of Iodides, Cuprous Iodide in

FORM OF DIRTY WHITE precipitate. Chlorides and Bromides are not thus precipitated. If clear starch paste is added to a solution of an Iodide in the cold, and Chlorine water added drop by drop, A BLUE COLOR WILL FORM FROM FORMATION OF IODIDE OF STARCH. Heat and an excess of Chlorine water removes the coloring. Any Iodide heated with conc. H_2SO_4 and MnO_2 liberates Iodine in the free form, giving beautiful violet vapors, which condense in dark brownish scales on the cooler portions of the tube. Solution of Mercuric Chloride added to an Iodide in solution, gives a SALMON COLORED PRECIPITATE, RAPIDLY BECOMING SCARLET, HgI_2 . Nitrate of Lead with solution of an Iodide gives beautiful yellow precipitate, slightly soluble in boiling water, but precipitated, as the water cools, in form of glistening yellow scales of PbI_2 .

HYDROSULPHURIC: Recognized easily by its characteristic odor. The acid and any of its soluble salts precipitate Lead salts from the solution in the form of brownish-black PbS . Paper moistened with Pb_2NO_3 when held in the gas or moistened with the solution of the gas is STAINED BROWN. $AgNO_3$ produces a black precipitate of Ag_2S , insoluble in NH_4HO oxidized (into Silver Sulphate) by HNO_3 , and dissolved.

Alkaline Sulphides are easily identified by action of a solution of Potassic Plumbate (formed by dissolving Pb_2NO_3 in excess of KHO). With normal Sulphides, the Plumbate GIVE AT ONCE A BLACK PRECIPITATE; WITH HIGHER SULPHIDES IT GIVES A BROWNISH-RED PRECIPITATE, BECOMING DARK BROWN TO BLACK in a short time.

Of the Silver salts of this Group, all are soluble in NH_4HO , except the Iodide and Ferrocyanide (yellowish-white,) and the Sulphide (black).

ACIDS IDENTIFIED BY FERRIC CHLORIDE.

While some of these Acids are precipitable by Nitrate of Silver, they are most easily identified by Salts of Iron.

HYDROFERROCYANIC: In solution of Ferrocyanides, Ferric Chloride gives a **DEEP BLUE PRECIPITATE** insoluble in HCl—Prussian Blue (Fe_4Fcy_3).
Solution of Copper Sulphate gives a **CHOCOLATE BROWN PRECIPITATE**— Cu_2FCy —insoluble in HCl, soluble in NH_4HO .

HYDROFERRICYANIC: In solution of Ferricyanides, Ferric Chloride gives a brownish-green coloration, but no precipitate. With **FERROUS SALTS** a **DEEP BLUE** precipitate, $\text{Fe}_3(\text{Fdcy})_2$ —Turnbull's Blue, insoluble in HCl.

The addition of SnCl_2 to a mixture of Ferric Chloride and Ferricyanide, gives instantly a blue precipitate from the reduction of Ferric to Ferrous Chloride.

TANNIC: With solution of Ferric Chloride forms a bluish-black (ink) precipitate.

GALLIC: Forms a precipitate similar to that of the Tannic Acid.

SULPHOCYANIC: With solution of Ferric Chloride, an **INTENSE BLOOD-RED COLORATION**, but no precipitate. **THE COLOR IS NOT CHANGED BY HCl EVEN WHEN BOILED, BUT QUICKLY DISCHARGED BY HgCl_2 .**

SULPHUROUS: With Ferric Chloride forms a **RED COLOR RAPIDLY DESTROYED BY BOILING WITH HCl.**

ACETIC: Acetates form a brownish-red color destroyed by HCl in the cold.

PHOSPHORIC: With Ferric Chloride a yellowish-white precipitate, insoluble in Acetic Acid.

**SUBSTANCES THAT DECOLORIZE SULPHATE OF
INDIGO.**

- | | |
|------------------------------------|---|
| 1. Without addition of an acid: | { Chlorine.
Hypochlorous Acid.
Chlorous Acid.
Hypochlorites.
Bromine.
Nitric Acid (not too dilute).
Alkaline Sulphides. |
| 2. On addition of HCl and heating: | { Chlorates.
Nitrates.
Iodates.
Bromates.
Manganates.
Manganic Oxide.
Plumbic Oxide. |

In applying this test enough of the Indigo solution is placed in water to give a blue color, and the substance is then dropped into the solution and the changes observed, which occur speedily if at all.

ACIDS NOT PRECIPITATED BY GROUP REAGENTS.

Crystals of Nitrates, Chlorates, Bromates and Iodates deflagrate on red-hot charcoal.

NITRIC: All normal nitrates are soluble: a few basic Nitrates (of Hg and Bi) are insoluble in water.

If a Nitrate is added to Sulphuric Acid and Copper, and the mixture heated, **NITRIC OXIDE IS EVOLVED AND THE AIR IN THE TEST TUBE BECOMES ORANGE-COLORED**; best seen by looking lengthways through the test tube.

If a Nitrate is added to conc. Sulphuric Acid, and a strong solution of Ferrous Sulphate carefully poured over the Acid without mixing the solutions, **A BROWN RING** will form between the two layers of liquid, best seen by reflected light. The color disappears on boiling, the NO. being expelled by heat.

If solution of Sulphate of Indigo is added to a Nitrate with HCl, the color does not disappear, but the color is discharged by boiling the mixture.

CHLORIC: Chlorates when heated red-hot give off Oxygen and are reduced to Chlorides, and then give reactions for Hydrochloric Acid.

When Chlorates are heated with conc. HCl. **A YELLOW GAS** is given off, which bleaches Indigo very powerfully.

BROMIC AND IODIC: When Bromates and Iodates are heated red-hot they give off Oxygen and are reduced to Bromides and Iodides, and then give reactions for Hydrobromic and Hydriodic acids respectively.

**ORGANIC ACIDS; EVOLVE COMBUSTIBLE GASES AND
BLACKEN BY (SEPARATION OF CARBON) WHEN
HEATED STRONGLY ON PLATINUM FOIL.**

Cyanogen compounds of the heavy metals will exhibit the same reactions.

ACETIC: The normal Acetates are all soluble in water: a few basic Acetates are insoluble. Acetic Acid has the characteristic odor of vinegar. If Sulphuric Acid is added to an Acetate and warmed the odor of Acetic Acid is evolved. If equal volumes of Sulphuric Acid and Alcohol are added to an Acetate and heated the fragrant odor of Acetic Ether is obtained. If an Acetate is added to neutral Ferric Chloride, a brownish red color appears from formation of Ferric Acetate. The color disappears at once when HCl is added (distinction from Sulphocyanides and Sulphides.)

TARTARIC: Chloride of Calcium from neutral solutions of the Tartarates throws down a white crystalline precipitate of Tartrate of Calcium, soluble in Acetic Acid (distinction from Oxalates.) Tartaric Acid added in excess to KHO precipitates "Cream Tartar" — $\text{KHC}_4\text{H}_4\text{O}_6$, white, crystalline, soluble in 180 parts of water. Thorough shaking promotes the formation of the precipitate.

VOLUMETRIC ANALYSIS.

Quantitative Chemical Analysis may be performed in two ways:

I. By separating and weighing the substance sought, either in the elementary form, or in some known state of chemical combination (gravimetric method).

II. By acting on the material to be analyzed by characteristic reagents of known strength, and from the volume of the reagent used, determining the amount of the substance present (volumetric method).

Suppose a dime weighs 2.5 grams and we require the amount of pure silver in the coin. After dissolving it in Nitric Acid, we may precipitate all the silver by a slip of sheet copper, separate and weigh the pure silver directly; or we may precipitate all the silver in the form of AgCl. by HCl., weigh the AgCl. and calculate the amount of silver from the known fact that every 143.5 parts of AgCl. contains 108 parts of silver. These processes illustrate the gravimetric method.

If we dissolve 58.5 grams of pure NaCl in water to measure 1000 c. c. and find that 20½ c. c. of this solution are required to completely precipitate all the silver in the coin, we determine that the dime contained 2.25 grams of silver, since 1 c. c. of the solution of Sodium Chloride will precipitate .108 grams of silver in the form of Chloride, and $20\frac{1}{2} \times .108 = 2.25$. This process illustrates the volumetric method.

Since we can measure more rapidly than we can weigh, and no time is required to wash and dry precipitates in Volumetric Analysis, the latter method is more rapid and exact than the gravimetric method in all cases where it can be used.

Volumetric Analysis requires the following conditions:

I. The reagent or test solution must produce a reaction of such a character that the termination can be instantly and unmistakably recognized by the eye. The indication may be revealed by change of color, the production or destruction of a color, the formation of a precipitate, &c.

II. A solution of a reagent whose chemical power is accurately known = "Standard Solution."

III. Graduated vessels for accurately delivering a given quantity of the Standard Solution, or for measuring the quantity used in any analysis. Pipettes for delivering a certain volume, and burettes for measuring quantity.

Classification of methods in Volumetric Analysis:

I. When the determination of the substance is effected by saturation with substance of opposite qualities, e. g., acids and alkalis.

II. Where the determination of a substance is effected by a reducing or oxidizing agent of known power: the reducing agents being F_2Cl_2 and $Na_2S_2O_3$; the oxidizing agents, $KMnO_4$, $KHCrO_4$, and I.

III. Where the determination of a substance is effected by precipitation, as in case of silver.

A NORMAL SOLUTION is the monatomic equivalent of the active substance in terms of grams, dissolved in water to measure 1000 c. c. A decinormal ($\frac{N}{10}$) and a centinormal ($\frac{N}{100}$) contain respectively the tenth and the hundredth part of the normal strength.

Normal Acid.

Prepare pure crystallized Oxalic Acid by re-crystallizing commercial acid. It must be free from any foreign substance, from adhering water and not effervesced. Weigh out 63 grams and dissolve in distilled water to make 1000 c.c. = Normal Acid. Oxalic Acid is used as the starting point in preparing a Standard solution, because it can be weighed directly, in consequence of its uniform composition and absence of tendency to change. Normal acids of Nitric, Sulphuric and Hydrochloric acids may be prepared, not by direct weighing, but by estimation of their strength by nominal alkaline solutions, and then reducing to the required strength by addition of water. Suppose 40 c.c. of HCl are added to 1000 c.c. of water, and 20 c.c. of this mixture placed in a beaker with 5 drops of Litmus solution, and exactly neutralized by normal alkaline solution. If this acid requires 20 c.c. of the normal alkaline solution for neutrality, it is a normal acid; but if it requires, say 28.5 c.c. it is too strong. $20:28.5::1000:1175$, and the 1000 c.c. contain enough acid to make 1175 c.c. of normal acid: by adding 175 c.c. of water to the 1000 c.c. of acid, a normal acid is formed. In the same way normal acids may be prepared from any of the stronger acids when once we have a normal alkaline solution to standardize the acids. Hydrochloric, Sulphuric, Nitric and Oxalic acids are to be chosen in the order named for ordinary use in alkalimetry.

Normal Alkaline Solutions.

These cannot be prepared by weighing out the required number of grams of the caustic alkali and dissolving in water, because the alkaline hydrates so rapidly absorb water and carbonic acid when exposed to the air. The normal solution is easily prepared by first dissolving an excess of the caustic hydrate in water, and then standardizing by normal Oxalic Acid, and then reducing with the required amount of water as pointed out in preparing normal HCl.

Caustic alkalis are better than carbonated alkalis for making normal solutions, because we avoid the disturbing influence of the carbonic acid set free by acids acting on carbonated alkalis.

Normal solutions made either with KHO, or NaHO, answer all the conditions required most admirably. They should be kept in bottles with ground glass stoppers, and the stoppers should be well coated with melted paraffine to make the bottle air-tight, and to prevent the stopper from sticking in the neck of the bottle.

The following table gives useful data for preparing normal solutions and for calculating the results in Volumetric Analysis:

Table for Normal Solutions and Analysis of Alkalies and Acids Volumetrically.

SUBSTANCE.	FORMULA.	ATOMIC WEIGHT.	Grams required to make 1000 c. c. Normal Solution	NORMAL FACTORS.*
Potassic Hydrate.....	KHO	56.1	56.1	0.2805
Potassic Carbonate.....	K ₂ CO ₃	138.2	69.1	0.3455
Potassic Bicarbonate.....	KHCO ₃	100.1	100.1	0.5005
Sodic Hydrate.....	NaHO	40	40	0.200
Sodic Carbonate.....	Na ₂ CO ₃	106	53	0.265
Sodic Bicarbonate.....	NaHCO ₃	84	84	0.420
Ammonia.....	NH ₃	17	17	0.085
Ammonic Carbonate.....	(NH ₄) ₂ CO ₃	96	48	0.240
Lime.....	CaO	56	28	0.140
Calcic Hydrate.....	Ca(HO) ₂	74	37	0.185
Calcic Carbonate.....	CaCO ₃	100	50	0.250
Nitric Acid.....	HNO ₃	63	63	0.315
Hydrochloric Acid.....	HCl	36.5	36.5	0.1825
Sulphuric Acid.....	H ₂ SO ₄	98	49	0.245
Oxalic Acid.....	H ₂ C ₂ O ₄ ·2H ₂ O	126	63	0.315
Acetic Acid.....	HC ₂ H ₃ O ₂	60	60	0.300
Tartaric Acid.....	H ₂ C ₄ H ₄ O ₆	150	75	0.375

* This is the factor by which the number of c.c. of Normal Solution used in any analysis is to be multiplied to find the per cent. of pure substance present in the material, when it has been weighed out in (monatomic) terms of grams, made up to 1000 c.c. with water, and 20 c.c. of the solution employed for analysis.

Indicators Used in Alkalimetry and Acidimetry.

Litmus Solution. Reduce litmus cubes to a coarse powder; boil this for ten minutes in thirty volumes of alcohol; pour off the alcohol and boil again with fresh alcohol: pour off all the alcohol, and pour on the purified litmus 100 volumes of cold distilled water and let it stand for two days: pour off the clear liquid and preserve this test solution in a bottle without a stopper. The residual litmus can be treated three or four times in succession with cold water to prepare a test solution. The solution is reddened by acids and blued by alkalies. Carbonic acid gives a wine-red, which may be removed by boiling or by prolonged stirring.

Cochineal Solution. Bruise ten grams of Cochineal and steep for two days in a litre of a mixture of three parts water and one part alcohol: pour off the clear solution and preserve in a stoppered bottle. The natural color of the solution is orange, but alkalies turn it purple: acids restore the orange color. It is less affected by carbonic acid than litmus, and hence valuable in titrating the carbonates: not so well suited for analysis of weak organic acids as litmus.

Turmeric Paper. Digest the coarsely powdered root repeatedly in small quantities of water to remove objectionable coloring matter, and then in dilute alcohol. Pour off the alcoholic solution and dip into this strips of white printing paper; dry these and keep them in the dark. Alkalies turn the paper brown. Turmeric paper is a very sensitive test with lime water, baryta, &c.

Alkalimetry.

Alkalimetry is the method of determining the amount of alkali present in any given substance, either in the state of caustic or carbonated alkali.

Weigh out the monatomic equivalent in terms of grams (see table for Normal Solutions) and dissolve in water to measure 1000 c.c. With a pipette measure out 20 c.c. and titrate with normal acid (with litmus or cochineal solution as an indicator) and multiply the c.c. of acid used by the normal factor to find the per cent. of pure substance present. Where duplicate analysis and accurate work are desired, this is the best method.

Another method is to weigh out a definite quantity of the substance dissolved in water and neutralized with normal acid, multiply the c.c. of acid used by the monatomic equivalent of the substance analyzed, and the product will be the number of milligrams of pure material in the substance. A litre of normal HCl will exactly neutralize 40 grams of NaHO: 1 c.c. will neutralize 40 milligrams of the same. By comparing the milligrams found with the grams of substance analyzed, the per cent. of pure material is readily determined.

If it is required to know the proportion of caustic and of carbonated alkali in any substance, weigh out say five grams and determine the total amount of alkaline substance; then weigh out five grams and place in a flask of definite measure, add an excess of BaCl_2 or CaCl_2 , pour in some water and boil, then fill up to the measure, draw an aliquot part of the clear solution and analyze this for the caustic alkali, and determine the total caustic alkali from the proportion of the solution used. The difference between caustic alkali and total alkali will represent the carbonated alkali.

In the Volumetric analysis of the alkaline earths and their carbonates, in consequence of their insolubility they are weighed and analyzed without previous solution. A weighed quantity is treated with an excess of normal HCl. to insure complete decomposition, and the solution boiled to expel carbonic acid and the acid solution is brought to neutral condition by normal alkaline solution. Subtract c.c. of normal alkali used from c.c. of acid employed, and the difference shows the c.c. of normal acid required to neutralize the alkaline earth. This method by residue is very convenient in analysis of most carbonates.

To determine the volumes of NH_3 in Ammonia water find the grams of NH_3 in 1000 c.c. then divide this by the weight of a litre of $\text{NH}_3 = .08936(\text{Crith}) \times 85$ (specific gravity of NH_3).

Acidimetry.

Acidimetry is the determination of the uncombined acid present in any substance.

Weigh out the number of grams equal to the monatomic equivalent of the acid, reduce with water to 1000 c.c., measure 20 c.c., neutralize with normal alkali, and multiply c.c. of normal alkali by normal factor for per cent. of pure acid.

A given weight of acid may be directly analyzed without reducing with water, the same as in alkalies.

If acid contains foreign coloring matter, e. g., vinegar, the point of neutrality is best determined by turmeric paper.

The volumes of HCl in a specimen of the acid may be determined by finding the number of grams in a litre and dividing this by $\text{crith} \times 18\frac{1}{2}$ (specific gravity of HCl.) The quotient will be the number of volumes of the gas dissolved in water to form the acid.

